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Cyanoacetylene and Its Derivatives: XXXIII.* One-Pot Stereoselective Synthesis of Bis-iminodihydrofurans from 4-Hydroxy-4-methyl-2-pentynonitrile and Aromatic Amines

B. A. Trofimov[1], A. G. Mal'kina[1], O. A. Shemyakina[1], R. N. Kudyakova[1], L. V. Sokolyanskaya[1], L. M. Sinegovskaya[1], A. I. Albanov[1], V. I. Smirnov[1], O. N. Kazheva[2], A. N. Chekhlov[2], and O. A. D'yachenko[2]

[1] *Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*

[2] *Institute of Chemical Physics Problems, Russian Academy of Sciences*

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Abstract—4-Hydroxy-4-methyl-2-pentynonitrile reacts with aniline, *N*-methylaniline, and 2-naphthylamine under mild conditions (20–80°C) to afford the corresponding 4-arylamino-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-5,5-dimethyl-2,5-dihydrofurans in one preparative step. According to the X-ray diffraction data, both imino groups in the products have *syn* configuration with respect to the ring oxygen atom.

Cyanoacetylene and its functional derivatives, in particular acetylenic hydroxy nitriles with the general formula $R^1R^2C(OH)C{\equiv}CCN$ [$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Et$; $R^1R^2 = (CH_2)_5$], may be regarded as latent prebiological structures capable of undergoing self-organization and self-assembly to give complex polyfunctional compounds related to sugars and natural antibiotics [2, 3]. Systematic studies on the additions of a wide series of nitrogen-containing nucleophiles (ammonia [4, 5], primary [6–8] and secondary amines [9], amino alcohols [10], azide ion [11], and some azoles [12–14]) to nitriles derived from α,β-acetylenic γ-hydroxy carboxylic acids led to the development of general procedures for the synthesis of 4-amino-2-iminodihydrofurans and aminoalkenonitriles, as well as of their azole analogs. We also reported [7, 8] on successive syntheses of mono-, bis-, tris-, and tetrakis-iminodihydrofurans from methylamine and 4-hydroxy-4-methyl-2-pentynonitrile. Tris-iminodihydrofuran was shown to be an effective luminophor [7, 8].

In the present article we report for the first time on the reaction of acetylenic hydroxy nitriles with aromatic amines, aniline, *N*-methylaniline, and 2-naphthylamine. This study was aimed at elucidating general relations holding in this reaction and obtaining new iminodihydrofuran derivatives. The 2-imino-2,5-dihydrofuran structure is related to 2,5-dihydrofuran-2-one fragment which constitutes a part of many natural molecules, in particular ascorbic, penicillic, and tetronic acids. Introduction of aromatic substituents into iminodihydrofuran molecules may be promising from the viewpoint of improving their biological activity and other parameters, e.g., luminescent properties which are important for creation of optoelectronic materials.

Our experiments showed that, unlike primary amines of the aliphatic series which add to 4-hydroxy-4-methyl-2-pentynonitrile (**I**) at room temperature in 1–2 h [6] with formation of 1:1 adducts, aniline reacts in succession with two molecules of **I** (molar reactant ratio 1:1, 20–25°C) to give an 1:2 adduct, bis-iminodihydrofuran **IV**, whose yield attains 42% in 30 days. Obviously, the imino group in the initially formed iminodihydrofuran **II** successfully competes with the amino group in aniline for the triple bond in cyanoalkyne **I**. As a result, alkenonitrile **III** is formed, and its subsequent cyclization yields bis-iminodihydrofuran **IV** (Scheme 1).

Further study has shown that the yield of **IV** increases to 54% under more severe conditions (acetonitrile, 75–80°C, 14 h). The ^{1}H NMR spectrum of the product mixture ($CDCl_3$) contains singlets at δ 1.43,

* For communication XXXII, see [1].

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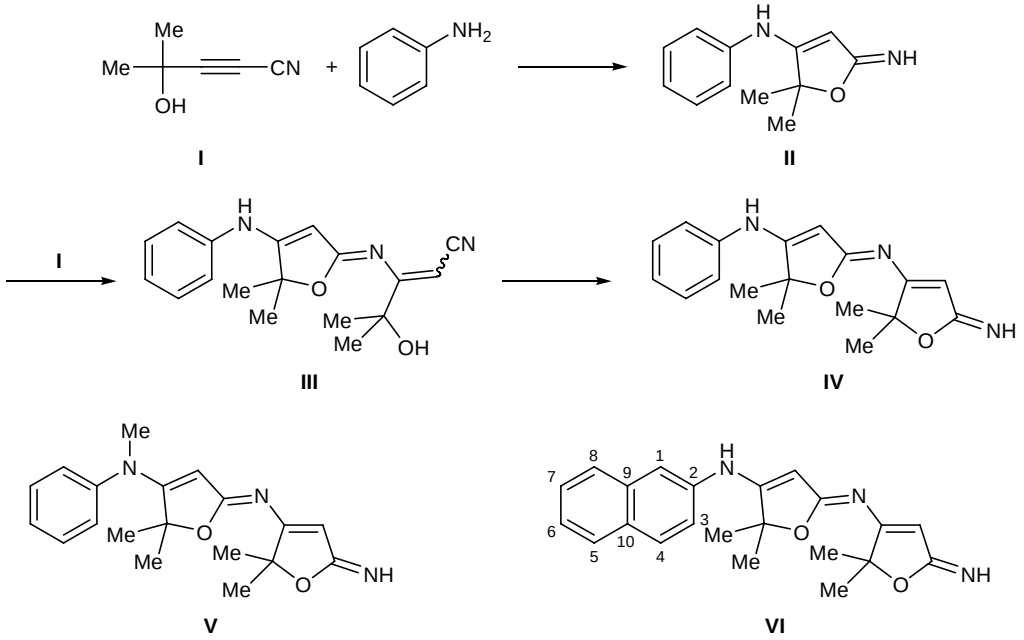
Scheme 1.



1.64 (Me), 5.49, and 5.53 ppm (C=CH) due to bis-iminodihydrofuran **IV** and those belonging to iminodihydrofuran **II** at δ 1.55 (s, Me) and 5.16 (s, C=CH), the ratio **IV**:**II** being equal to 5:1. Our attempts to isolate iminodihydrofuran **II** by column chromatography or crystallization always led to a sample containing a small amount of compound **IV**. Iminodihydrofuran **II** was present in the reaction mixture when cyanoalkyne **I** was taken in a twofold excess with respect to aniline.

N-Methylaniline is a stronger base than aniline (pK_a 4.85 and 4.58, respectively) [15]; therefore, it was expected to react with compound **I** under milder conditions. However, the reaction was not complete even in 20 h at 80°C. The IR spectrum of the reaction mixture revealed absorption bands due to initial cyanoalkyne **I** (2285–2265 cm^{-1}, C≡C–CN) and cyanoalkene **III** (2200 cm^{-1}). The formation of bis-iminodihydrofuran **V** was complete only when the reaction mixture was additionally kept for 30 days at room temperature. We can conclude that steric hindrances to the addition at the triple bond of **I**, created by the *N*-methyl group, are more significant than slight increase in the basicity.

2-Naphthylamine reacted with compound **I** according to similar scheme (acetonitrile, 75–80°C, 40 h), and the only product was bis-iminodihydrofuran **VI** (yield 56%).

Compounds **IV**–**VI** are yellow crystalline substances which are soluble in most organic solvents and insoluble in water. The IR spectra of their solutions in $CHCl_3$ (*c* = 0.01–0.02 M; *d* = 0.5, 1, and 2 cm) contained absorption bands due to stretching vibrations of the =N–H (3300 cm^{-1}) and NH groups (3418 cm^{-1}; **IV**, **VI**), while no absorption assignable to cyano or hydroxy group was present. Bis-iminodihydrofurans **IV**–**VI** showed in the ^{1}H NMR spectra ($CDCl_3$) two singlets at δ 5.05–5.66 ppm from the olefinic protons, singlets at δ 1.39–1.66 ppm from the methyl protons, and aromatic proton signals in the region δ 7.12–7.80 ppm. The ^{13}C NMR spectra also confirmed conformational homogeneity of the products.

The structure of 4-anilino-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-5,5-dimethyl-2,5-dihydrofuran (**IV**) in the crystalline state was proved by the X-ray diffraction data. The atom numbering is shown in Fig. 1, and the principal bond lengths and bond angles are given in Tables 1 and 2. Molecules **IV** in crystal (Fig. 2) give rise to zigzag chains along the *b* axis due to formation of intermolecular hydrogen bonds N–H···N with the following parameters: N^1–H^1 0.89(2) Å, $H^1\cdots N^{3*}$ 1.99(2) Å, $\angle N^1$–$H^1\cdots N^{3*}$ 167.2° (* stands for symmetry operation $-x$, $0.5 + y$, $0.5 - z$). The most important result was that we were the first to determine the configuration of the imino groups (*syn* with respect to the oxygen atom in the furan ring) in the iminodihydrofuran fragments formed by intramolecular cyclization of intermediate hydroxyalkenonitriles **III**. This reaction provides a typical example of completion of attack by many nucleophiles on the C≡C

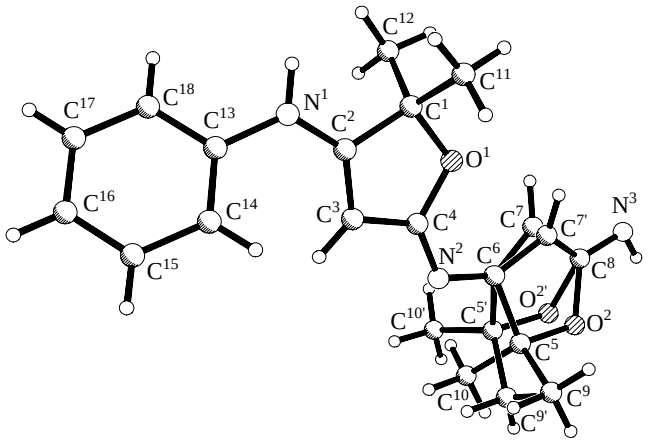
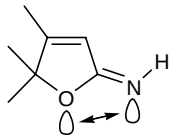


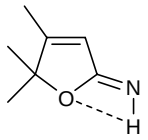
Fig. 1. Structure of the molecule of 4-anilino-5,5-dimethyl-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-2,5-dihydrofuran (**IV**) according to the X-ray diffraction data. Statistically disordered atoms are denoted with primed indices.

bond in cyanoacetylenic alcohols like compound **I** and its homologs [3]. However, the stereochemistry of the subsequent attack by the hydroxy group on the cyano group remained so far unknown. Now, we can state with certainty that the formation of iminodihydrofuran structures by cyclization of hydroxyalkenonitriles **III** is a stereoselective process resulting in *syn* configuration of the imino groups with respect to the oxygen atom. A probable reason is repulsive interaction between unshared electron pairs on the oxygen and nitrogen atoms in the *anti* conformation (structure **A**).

An additional factor stabilizing the *syn* configuration may be intramolecular hydrogen bond O···H–N= (structure **B**), though such bonds (four-membered ring) are usually weak. The possibility for hydrogen bonding between the furan oxygen atom and imino group



A



B

follows from the intramolecular distances $H^3\cdots O^2$ 2.32 and 2.26 Å, which are appreciably shorter than usual intermolecular H···O contacts (2.45 Å) [16], as well as from the reduced $H^3N^3C^8$ angle [108.2° instead of expected 120°; for comparison, the bond angle $C^4N^2C^6$ is 121.8(2)°].

Refinement of the crystalline structure showed that the O^2, C^5 (with methyl groups C^9 and C^{10}), and C^7 atoms in molecule **IV** are statistically disordered by two positions at a ratio of 0.6:0.4 (Fig. 1; the atoms in the second position are denoted with primed indices). This means that the crystalline structure is formed by packing of molecules **IV** in two conformations at a ratio of 3:2. As seen from Fig. 1, the only difference between the above conformers is that the terminal heterorings therein are turned through different angles about the axis passing through the C^6 and C^8 atoms. We believe that the observed conformational dualism does not affect the mechanism of chemical reactions of compound **IV**; however, it may be interesting for conformational and quantum-chemical calculations.

Treatment of compounds **IV** and **VI** with gaseous hydrogen chloride gave 92–95% of salts **VII** and **VIII** via protonation of two nitrogen atoms (Scheme 2). Dihydrochlorides **VII** and **VIII** are beige powders which melt with decomposition and are soluble in alcohol and DMSO. The IR spectra of **VII** and **VIII** contain a broad absorption band in the region 2500–

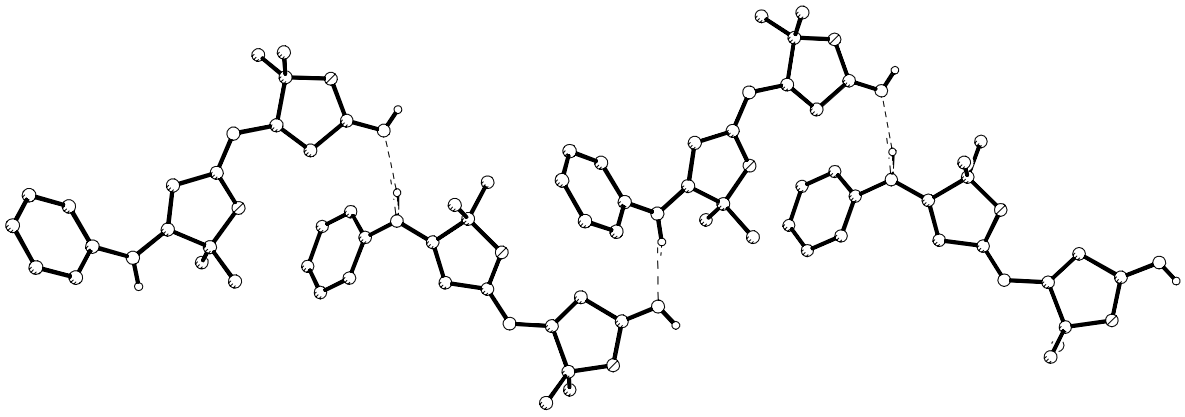
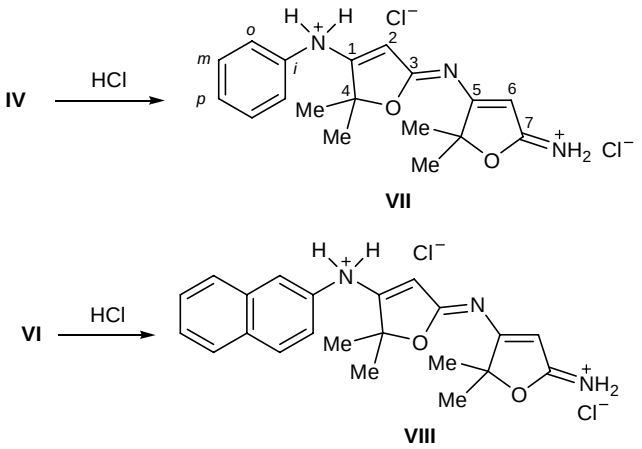


Fig. 2. Fragment of the crystalline structure of compound **IV**: packing of molecules along the crystallographic *b* axis and intermolecular hydrogen bonds N–H···N. For the sake of clarity, only one conformation and hydrogen atoms attached to nitrogen are shown.

Scheme 2.



3130 cm^{-1} typical of ammonium salts [17]. Their structure is also confirmed by the ^1H and ^{13}C NMR spectra.

The electron absorption spectra of bis-iminodihydrofurans **IV** and **VI**, as well as of 2,5-dihydro-2-(2,5-dihydro-2-imino-5,5-dimethyl-4-furylimino)-5,5-dimethyl-4-methylaminofuran (**IX**) [7, 8] taken for comparison, are characterized by a strong band in the visible region, ν 32260–22220 cm^{-1} (Table 3). Introduction of aromatic substituents, such as phenyl or naphthyl group, leads to a red shift of this band. Compounds **IV** and **VI** showed a strong fluorescence with a quantum yield comparable with that of bis-iminodihydrofuran **IX** (φ = 0.79). Bis-iminodihydrofuran **IV** is also characterized by a large red shift of the fluorescence band. The Stokes shift found for a solution of **IV** in alcohol is 6865 cm^{-1}, which suggests change of the geometric parameters of this compound in the excited state.

Thus we have synthesized polyconjugated heterocyclic systems, arylamino-substituted bis-iminodihydrofurans by cascade reactions of 4-hydroxy-4-methyl-2-pentynonitrile (**I**) with aniline, *N*-methylaniline and 2-naphthylamine in a one-pot procedure. The products are promising as building blocks for fine organic synthesis and as potential biologically active substances, and the developed approach may be used in the design of new materials for optoelectronics [18].

EXPERIMENTAL

The IR spectra were recorded on Specord 75IR and Bruker IFS-25 spectrometers from samples prepared as KBr pellets and solutions in $CHCl_3$ ($c \approx 0.01$ M, d = 0.5–5 cm). The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument (400 MHz) in $CDCl_3$ (compounds **IV**–**VI**) and DMSO-d_6 (**VII**, **VIII**) using HMDS as internal reference. The UV spectra were obtained on a Perkin–Elmer Lambda 35 UV-Vis Spectrometer from solutions in alcohol.

Fluorescence studies were performed using solutions in methanol with a concentration of $(2–5)\times 10^{-5}$ M and poly(2,5-dimethyl-1-pyrazolylvinyl) films. Films were prepared by applying solutions of compounds to a quratz support, followed by drying under reduced pressure at 20°C. A DKsSh-1000 xenon lamp was used as excitation source. Its light flux was monochromated using an MDR-2 setup and was directed

Table 1. Bond angles in the molecule of 4-anilino-5,5-dimethyl-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-2,5-dihydrofuran (**IV**)

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C^2N^1C^{13}$	124.8(2)	$N^2C^4O^1$	124.0(2)	$N^3C^8C^7$	127.7(5)	$C^{9'}C^{5'}C^{10'}$	113.4(9)
$C^4N^2C^6$	121.8(2)	$N^2C^4C^3$	125.7(2)	$O^2C^8C^7$	108.2(5)	$O^{2'}C^{5'}C^6$	103.7(5)
$C^4O^1C^1$	109.3(2)	$O^1C^4C^3$	110.3(2)	$C^8O^2C^5$	110.6(4)	$C^{9'}C^{5'}C^6$	106.4(9)
$O^1C^1C^{11}$	107.8(2)	$C^7C^6N^2$	134.4(5)	$O^2C^5C^{10}$	108.5(4)	$C^{10'}C^{5'}C^6$	117.2(6)
$O^1C^1C^2$	102.4(2)	$C^{7'}C^6N^2$	139.7(7)	$O^2C^5C^6$	101.8(4)	$C^6C^{7'}C^8$	112.6(8)
$C^{11}C^1C^2$	113.0(2)	$C^7C^6C^5$	112.1(5)	$C^{10}C^5C^6$	109.0(6)	$C^{14}C^{13}C^{18}$	119.8(2)
$O^1C^1C^{12}$	107.3(1)	$N^2C^6C^5$	113.2(3)	$O^2C^5C^9$	107.8(4)	$C^{14}C^{13}N^1$	122.3(2)
$C^{11}C^1C^{12}$	112.5(2)	$C^{7'}C^6C^{5'}$	105.0(7)	$C^{10}C^5C^9$	111.8(6)	$C^{18}C^{13}N^1$	117.8(2)
$C^2C^1C^{12}$	113.0(2)	$N^2C^6C^{5'}$	114.8(3)	$C^6C^5C^9$	117.2(4)	$C^{13}C^{14}C^{15}$	119.5(3)
$C^3C^2N^1$	131.3(2)	$N^3C^8C^{7'}$	129.8(7)	$C^6C^7C^8$	106.7(5)	$C^{16}C^{15}C^{14}$	119.7(3)
$C^3C^2C^1$	109.1(2)	$N^3C^8O^2$	123.5(3)	$C^8O^{2'}C^{5'}$	107.1(5)	$C^{17}C^{16}C^{15}$	120.5(3)
$N^1C^2C^1$	119.6(2)	$N^3C^8O^{2'}$	117.4(3)	$O^{2'}C^{5'}C^{9'}$	108.9(7)	$C^{16}C^{17}C^{18}$	119.9(3)
$C^2C^3C^4$	108.9(2)	$C^{7'}C^8O^{2'}$	111.4(8)	$O^{2'}C^{5'}C^{10'}$	106.6(6)	$C^{17}C^{18}C^{13}$	120.5(3)

Table 2. Bond lengths in the molecule of 4-anilino-5,5-dimethyl-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-2,5-dihydrofuran (**IV**)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O^1–C^1	1.464(2)	N^2–C^4	1.288(3)	C^5–C^6	1.506(6)	C^7–C^8	1.48(1)
O^1–C^4	1.352(2)	N^2–C^6	1.373(3)	C^5–C^9	1.511(8)	$C^{7'}$–C^8	1.38(2)
O^2–C^5	1.456(5)	N^3–C^8	1.263(3)	C^5–C^{10}	1.504(8)	C^{13}–C^{14}	1.377(3)
O^2–C^8	1.380(5)	C^1–C^2	1.513(3)	$C^{5'}$–C^6	1.614(9)	C^{13}–C^{18}	1.387(3)
$O^{2'}$–$C^{5'}$	1.450(7)	C^1–C^{11}	1.508(3)	$C^{5'}$–$C^{9'}$	1.50(1)	C^{14}–C^{15}	1.398(3)
$O^{2'}$–C^8	1.417(7)	C^1–C^{12}	1.524(3)	$C^{5'}$–$C^{10'}$	1.50(1)	C^{15}–C^{16}	1.379(4)
N^1–C^2	1.350(3)	C^2–C^3	1.343(3)	C^6–C^7	1.33(1)	C^{16}–C^{17}	1.369(4)
N^1–C^{13}	1.407(3)	C^3–C^4	1.417(3)	C^6–$C^{7'}$	1.34(2)	C^{17}–C^{18}	1.373(3)

with a condenser at an angle of 90° to a quartz cell containing a solution to be studied or at an angle of 45° to a film. Sample emission was scanned using another MDR-2 monochromator, and the signal was passed through an FEU-79A photoelectron multiplier and a YS-6 amplifier to a two-coordinate recorder. The luminescence quantum yield (φ) was determined by the relative procedure [19]. An alcoholic solution of bis-iminodihydrofuran **IX** was used as reference (φ = 0.79) [7, 8].

X-Ray analysis of compound **IV** was performed on an Enraf–Nonius CAD-4 diffractometer (MoK_α irradiation, graphite monochromator, ω/2θ scanning) at room temperature.

Aniline, *N*-methylaniline, and 2-naphthylamine were commercial products. 4-Hydroxy-4-methyl-2-pentynonitrile was synthesized by the procedure described in [20].

The progress of reactions was monitored by thin-layer chromatography on Al_2O_3 using chloroform–benzene–ethanol (20:4:1) as eluent.

4-Anilino-5,5-dimethyl-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-2,5-dihydrofuran (IV). *a*. A solution of 0.27 g (2.5 mmol) of alkyne **I** in 2 ml of acetonitrile was slowly added at 20–25°C to a solution of 0.23 g (2.5 mmol) of aniline in 2 ml of acetonitrile. The mixture was left to stand for 30 days, the solvent was removed under reduced pressure, the tarry residue was treated with a small amount of diethyl ether, and the yellow powder was filtered off through a glass filter, washed with diethyl ether, and dried under reduced pressure. Yield 0.16 g (42%), mp 200–202°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 690 m, 740 w, 770 m, 930 m, 960 m, 1078 s, 1139 s, 1178 s, 1259 s, 1295 w, 1340 w, 1360 m, 1372 s, 1439 s, 1486 s, 1513 br.s, 1574 s, 1600 m, 1656 s, 2926 w, 2977 m, 3285 m, 3530–3370 br.m. ^{1}H NMR spectrum, δ, ppm: 1.43 s and 1.64 s (12H, 4Me); 5.49 s and 5.54 s (2H, =CH); 7.12 t, 7.20 d, and 7.34 t (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 25.10, 25.60, 25.67 (**Me**$_2$C); 86.27, 88.71 (Me$_2$**C**); 100.46 (=CH); 120.12, 129.27 (C^o, C^m); 123.55 (C^p); 140.00 (C^i); 167.09, 170.91 (N–C=); 172.28, 173.28 (N=C). Found, %: C 69.49; H 6.87; N 13.50. $C_{18}H_{21}N_3O_2$. Calculated, %: C 69.45; H 6.80; N 13.49.

Table 3. Electron absorption and fluorescence spectra and fluorescence quantum yields (φ) of compounds **IV**, **VI**, **VII**, and **IX**

Comp. no.	Absorption, ν_{max}, cm^{-1}	Fluorescence, ν_{max}, cm^{-1}	Quantum yield φ	Stokes shift $\Delta\nu_{max}$, cm^{-1}
IV	27700	20835	0.39	6865
VI	26625	25975	0.68	650
VII	26182	23810	0.42	2372
IX[a]	27780	25450	0.79	2300

[a] Data of [7, 8].

Principal crystallographic parameters: $C_{18}H_{21}N_3O_2$; *M* 311.38; light yellow rhombic crystals; space group *Pbca*; *a* = 11.366(4), *b* = 15.725(2), *c* = 19.700(5) Å; *V* = 3521.0(2) Å^3; *Z* = 8; d_{calc} = 1.18 g/cm^3; μ(MoK_α) = 0.078 mm^{-1}. Intensities of 2230 independent reflections were measured; $2\theta_{max}$ = 44.94°; *h*, *k*, *l* ranges: $0 \le h \le 12$, $0 \le k \le 16$, $0 \le l \le 21$. The structure was solved by the direct method followed by Fourier syntheses using SHELXS-97 software [21] and was refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms using SHELXL-97 [22]. The final divergence factors *R* were equal to 0.043 [from 1720 reflections with $F_0 > 4\sigma(F_0)$] and 0.057 (from all 2230 reflections). The coordinates of the H^1 and H^3 atoms (attached to N^1 and N^3, respectively) were determined experimentally. The

other hydrogen atoms were localized from the geometry considerations. Additional information is available from the authors.

b. A solution of 0.55 g (5 mmol) of alkyne **I** in 5 ml of acetonitrile was added to a solution of 0.47 g (5 mmol) of aniline in 5 ml of acetonitrile, and the mixture was heated for 14 h at 80°C. It was then treated as described above in *a*. Yield 0.4 g (51%).

The solvent was removed from the filtrate on a rotary evaporator. Addition of a small amount of diethyl ether to the dark red tarry residue led to formation of a yellow powder which was filtered off, washed with diethyl ether, and dried under reduced pressure. The product, 0.14 g, was subjected to thin-layer chromatography on Al_2O_3 using chloroform–benzene–ethanol (20:4:1) as eluent to isolate 0.1 g of a mixture of compounds **II** and **IV** at a ratio of 3:1 (according to the ^{1}H NMR data). Overall yield of **IV** 54%. ^{1}H NMR spectrum, δ, ppm: compound **II**: 1.55 s (6H, Me), 5.16 s (1H, C=CH); compound **IV**: 1.43 s and 1.64 s (12H, Me), 5.49 s and 5.54 s (2H, C=CH); 7.06–7.34 m (H_{arom}).

c. A solution of 0.22 g (2 mmol) of alkyne **I** in 2 ml of acetonitrile was slowly added at 20–25°C to a solution of 0.09 g (1 mmol) of aniline in 2 ml of acetonitrile, and the mixture was left to stand for 21 days at room temperature. The solvent was removed under reduced pressure (water-jet pump), and the residue was treated as described above in *a* to isolate 0.13 g of a yellow powder (mp 180–190°C) containing compounds **II** and **IV** at a ratio of 1:4 (according to the ^{1}H NMR data).

2-(2-Imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-4-[methyl(phenyl)amino]-5,5-dimethyl-2,5-dihydrofuran (V). A solution of 0.27 g (2.5 mmol) of alkyne **I** in 5 ml of acetonitrile was added to a solution of 0.27 g (2.5 mmol) of *N*-methylaniline in 5 ml of acetonitrile, and the mixture was heated for 20 h at 80°C and was then kept for 30 days at 20–25°C. The mixture was treated as described above for compound **IV**, method *a*. Yield 0.13 g (33%), mp 140–142°C. IR spectrum, ν, cm^{-1}: 770 w, 810 w, 900 w, 950 w, 975 m, 1060 m, 1110 m, 1175 m, 1275 m, 1300 w, 1365 m, 1440 w, 1480 m, 1535 s, 1590 s, 1655 m, 2920 w, 2960 w, 3190 m, 3470–3370 br.m. ^{1}H NMR spectrum, δ, ppm: 1.39 s and 1.43 s (12H, Me), 3.28 s (3H, MeN), 5.05 s and 5.60 s (2H, =CH), 7.23 m and 7.41 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 25.09, 26.42 (**Me**$_2$C); 87.74 (Me$_2$**C**); 100.01 (=CH); 127.69, 129.35 (C^o, C^m); 128.36 (C^p); 143.86 (C^i); 157.51 (N–C=); 171.89, 172.98 (C=N). Found, %: C 67.23; H 7.19; N 12.26. $C_{19}H_{23}N_3O_2$. Calculated, %: C 70.13; H 7.12; N 12.90.

2-(2-Imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-4-naphthylamino-5,5-dimethyl-2,5-dihydrofuran (VI). A solution of 0.11 g (1 mmol) of alkyne **I** in 2 ml of acetonitrile was added to a solution of 0.14 g (1 mmol) of 2-naphthylamine in 3 ml of acetonitrile, and the mixture was heated for 40 h at 70°C. It was then treated as described above for compound **IV**, method *a*. Yield 0.10 g (56%), mp 213–215°C. IR spectrum, ν, cm^{-1}: 670 w, 733 w, 768 m, 933 m, 953 m, 1075 m, 1139 m, 1179 m, 1251 m, 1285 m, 1349 m, 1368 m, 1495 s, 1526 s, 1572 s, 1642 m, 2929 w, 2972 w, 3520–3460 br.w. ^{1}H NMR spectrum, δ, ppm: 1.49 s and 1.66 s (12H, Me), 5.62 s and 5.66 s (2H, =CH), 7.31–7.34 d.d (4-H), 7.41 t and 7.47 t (2H, 7-H, 6-H), 7.60 s (1H, N^{1}H), 7.72 d (1H, N^{3}H), 7.80 m (2H, 8-H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 25.22, 25.78 (**Me**$_2$C); 87.20, 88.73 (Me$_2$**C**); 100.00 br.s (=CH); 117.09 (C^6); 120.51 (C^7); 125.55 (C^1); 127.08, 127.30, 127.80 (C^5, C^8, C^4); 129.60 (C^3); 130.72 (C^9); 133.87 (C^{10}); 137.53 (C^2); 166.54 (=C–N); 171.34, 173.22 (C=N). Found, %: C 73.63; H 6.31; N 11.26. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63.

4-Anilino-5,5-dimethyl-2-(2-imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-2,5-dihydrofuran dihydrochloride (VII). Gaseous hydrogen chloride was passed over a period of 5 h through a solution of 0.10 g (0.32 mmol) of compound **IV** in 4 ml of anhydrous dioxane, maintained at 20–25°C. The solvent was removed under reduced pressure, and the residue was washed with dry diethyl ether. Yield 0.11 g (92%), decomposition point 276–278°C. IR spectrum, ν, cm^{-1}: 507 w, 531 w, 604 w, 656 w, 693 w, 737 w, 762 m, 814 m, 959 w, 1002 m, 1094 m, 1111 m, 1140 w, 1173 s, 1262 s, 1305 m, 1409 s, 1456 m, 1526 s, 1570 s, 1604 s, 1696 m, 2500–3130 br.s. ^{1}H NMR spectrum, δ, ppm: 1.64 s and 1.85 s (12H, Me), 5.95 s and 6.09 s (2H, =CH), 7.29 t and 7.46 m (5H, H_{arom}), 10.44 br.s and 12.04 s (4H, NH_2^+). ^{13}C NMR spectrum, δ_C, ppm: 24.00 (**Me**$_2$C^8), 24.70 (**Me**$_2$C^4); 84.16 (=**C**HC^2); 93.04 (C^8); 94.04 (=**C**HC^6); 122.07, 129.69 (C^o, C^m); 126.57 (C^p); 138.42 (C^i); 175.42 (C^3); 176.84 (C^7). Found, %: C 56.02; H 6.02; Cl 17.69; N 11.12. $C_{18}H_{21}N_3O_2 \cdot 2HCl$. Calculated, %: C 56.26; H 6.03; Cl 18.45; N 10.93.

2-(2-Imino-5,5-dimethyl-2,5-dihydro-4-furylimino)-4-naphthylamino-5,5-dimethyl-2,5-dihydrofuran dihydrochloride (VIII) was obtained in a similar way from 0.05 g (0.14 mmol) of compound **VI**. Yield 0.055 g (95%), decomposition point 270–272°C.

IR spectrum, ν, cm^{-1}: 477 w, 518 w, 668 w, 755 w, 788 w, 814 w, 959 w, 998 w, 1105 w, 1130 w, 1172 m, 1265 w, 1304 w, 1407 s, 1529 s, 1569 m, 1590 m, 1608 m, 1694 m, 2500–3130 br.s. ^{1}H NMR spectrum, δ, ppm: 1.69 s and 1.92 s (12H, Me), 6.19 s (2H, =CH), 7.55 m (6-H, 7-H), 7.66 d (4-H), 7.95 m (1-H, 5-H, 8-H), 8.03 d (N^3H), 10.58 and 12.07 (NH_2^+). ^{13}C NMR spectrum, δ_C, ppm: 24.25, 24.91 (Me); 85.11, 93.80 (=CH); 92.81, 94.75 (Me_2**C**); 119.14 (C^6); 121.43 (C^7); 126.46 (C^1); 127.22 (C^5, C^8); 127.98 (C^4); 129.42 (C^2); 131.05 (C^9); 133.19 (C^{10}); 136.19 (C^2). Found, %: C 60.45; H 5.33; Cl 15.40; N 10.52. $C_{22}H_{23}N_3O_2 \cdot 2HCl$. Calculated, %: C 60.83; H 5.80; Cl 16.32; N 9.67.

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REFERENCES

1. Mal'kina, A.G., Sokolyanskaya, L.V., Kudyakova, R.N., Sinegovskaya, L.M., Albanov, A.I., Shemyakina, O.A., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 61.
2. Trofimov, B.A., Mal'kina, A.G., and Skvortsov, Yu.M., *Zh. Org. Khim.*, 1993, vol. 29, p. 1268.
3. Trofimov, B.A. and Mal'kina, A.G., *Heterocycles*, 1999, vol. 51, p. 2485.
4. Skvortsov, Yu.M., Mal'kina, A.G., Trofimov, B.A., Volkov, A.N., and Bzhezovskii, V.M., *Zh. Org. Khim.*, 1981, vol. 17, p. 884.
5. Skvortsov, Yu.M., Mal'kina, A.G., Trofimov, B.A., Volkov, A.N., Kositsyna, E.I., and Voronov, V.K., *Zh. Org. Khim.*, 1982, vol. 18, p. 59.
6. Skvortsov, Yu.M., Fartysheva, O.M., Mal'kina, A.G., Kositsyna, E.I., Kashik, T.V., Ponomareva, S.M., Sigalov, M.V., and Trofimov, B.A., *Zh. Org. Khim.*, 1986, vol. 22, p. 255.
7. Trofimov, B.A., Mal'kina, A.G., Skvortsov, Yu.M., Sokolyanskaya, L.V., Smirnov, V.I., and Kositsyna, E.I., *Dokl. Akad. Nauk SSSR*, 1991, vol. 318, p. 1395.
8. Trofimov, B.A., Mal'kina, A.G., Skvortsov, Yu.M., Sokolyanskaya, L.V., Smirnov, V.I., and Kositsyna, E.I., *Zh. Org. Khim.*, 1992, vol. 28, p. 881.
9. Skvortsov, Yu.M., Mal'kina, A.G., Moshchevitina, E.I., Kositsyna, E.I., and Trofimov, B.A., *Zh. Org. Khim.*, 1992, vol. 28, p. 1371.
10. Skvortsov, Yu.M., Mal'kina, A.G., Sokolyanskaya, L.V., Kositsyna, E.I., Kukharev, B.F., and Gritsa, A.I., *Zh. Org. Khim.*, 1991, vol. 27, p. 526.
11. Trofimov, B.A., Mal'kina, A.G., and Kudyakova, R.N., *Zh. Org. Khim.*, 1993, vol. 29, p. 1942.
12. Skvortsov, Yu.M., Mal'kina, A.G., Trofimov, B.A., Kositsyna, E.I., Voronov, V.K., and Baikalova, L.V., *Zh. Org. Khim.*, 1984, vol. 20, p. 1108.
13. Skvortsov, Yu.M., Mal'kina, A.G., Trofimov, B.A., Volkov, A.N., Glazkova, N.P., and Proidakov, A.G., *Zh. Org. Khim.*, 1982, vol. 18, p. 983.
14. Mal'kina, A.G., Nosyreva, V.V., Kositsyna, E.I., and Trofimov, B.A., *Russ. J. Org. Chem.*, 1997, vol. 33, p. 399.
15. Albert, A. and Serjeant, E., *Ionization Constants of Acids and Bases*, London: Methuen, 1962. Translated under the title *Konstanty ionizatsii kislot i osnovanii*, Moscow: Khimiya, 1964, p. 139.
16. Zefirov, Yu.V. and Zorkii, P.M., *Usp. Khim.*, 1995, vol. 64, p. 446.
17. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972. Translated under the title *Sputnik khimika*, Moscow: Mir, 1976, pp. 210.
18. Hayes, R.T., Wasielevski, M.R., and Gosztola, D., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 5563.
19. Parker, C.A., *Photoluminescence of Solutions. With Applications to Photochemistry and Analytical Chemistry*, Amsterdam: Elsevier, 1968. Translated under the title *Fotolyuminestsentsiya rastvorov*, Moscow: Mir, 1972, p. 247.
20. Landor, S.R., Demetrion, B., Grzeskowiak, R., and Pavey, D., *J. Organomet. Chem.*, 1975, vol. 93, p. 129.
21. Sheldrick, G.M., *SHELXS-97. Program for Crystal Structure Determination*, Göttingen: Univ. of Göttingen, Germany, 1997.
22. Sheldrick, G.M., *SHELXL-97. Program for the Refinement of Crystal Structures*, Göttingen: Univ. of Göttingen, Germany, 1997.