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Synthesis and Properties of Furazanyl-Substituted Acetylenes and Diacetylenes*

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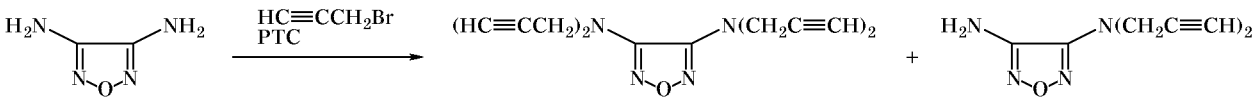
Abstract—Compounds of the acetylene and diacetylene series, containing a furazan ring, were synthesized by alkylation of 3,4-diaminofurazan and nucleophilic substitution of the nitro group in 3-amino-4-nitrofurazan under conditions of phase-transfer catalysis.

Studies of acetylene and its derivatives acquire increasing importance in the development of modern experimental and theoretical chemistry [3]. Under conditions of growing deficit of petroleum, elaboration of new methods for preparation of organic compounds from acetylene and synthesis of new, previously unknown acetylene derivatives becomes an urgent problem. High reactivity of compounds possessing a triple bond makes it possible to obtain therefrom various products of fine organic synthesis. Introduction of a triple bond as structural unit into natural and synthetic products often enhances their biological activity, extends the scope of pharmacological applications, and reduces their toxicity. Moreover, acetylene compounds are of great interest for the chemistry and material science of high-energy substances, for the triple bond possesses a great internal energy. On the other hand, furazan (1,2,5-oxadiazole) derivatives are used as pharmaceuticals, analytical reagents, propellants and explosives, and starting materials in organic synthesis, as well as for synthesis and modification of polymeric materials. The synthesis and chemical transformations of furazan derivatives have been reviewed in detail in [4, 5].

Compounds of the acetylene and diacetylene series, containing a furazan ring, have not been reported previously. The goal of the present work was to develop methods for preparation of compounds possessing both these fragments. Undoubtedly, such products are of interest from the viewpoints of both synthetic organic chemistry and possible practical applications.

As starting compounds we used 3,4-diaminofurazan (**I**) [6] and 3-amino-4-nitrofurazan (**II**) [7]. According to published data [8], 3,4-diaminofurazan (**I**) is a very weak base: its pK_{a1} value ranges from –1.94 to –4.46, i.e., it is lower by 7–9 log units than the corresponding parameter of aniline. Therefore, compound **I** reacts neither with dimethyl sulfate nor with ethyl bromide under usual conditions. Weak bases with pK_a ≪ 1 are alkylated taking advantage of their high NH acidity, i.e., the ability to generate N-anion by the action of bases. This process can be effected either via metalation (as shown in [9, 10]) or under conditions of

Scheme 1.



I **III** **IV**

PTC stands for phase-transfer catalysis: KOH, K_2CO_3, Bu_4NI, THF.

* For preliminary communications, see [1, 2].

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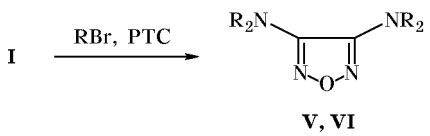
phase-transfer catalysis (PTC) [11]. The high NH acidity of 3,4-diaminofurazan (**I**) allowed us to perform its alkylation in the two-phase system KOH/K_2CO_3–dry THF using tetrabutylammonium iodide as phase-transfer catalyst.

3,4-Diaminofurazan (**I**) was brought into reaction with 2-propynyl bromide at a ratio of 1:4. As soon as 1 h after, we isolated 50% of exhaustive alkylation product **III** and 11% of *N*,*N*-dialkylated furazan **IV**. The structure of the products was proved by spectral data given in Table 1. Table 2 contains their yields, melting points (or refractive indices for liquids), and analytical data. The unsymmetrical structure of compound **IV** follows from its ^{13}C NMR spectrum which contains two signals from carbon atoms of the furazan ring at δ_C 151.56 and 149.80 ppm; symmetrically substituted furazan **III** gives only one signal at δ_C 152.20 ppm. In the ^1H NMR spectrum of **IV** we observed a broadened singlet at δ 4.23 ppm from protons of the amino group; the latter gives rise to IR absorption at 3450 and 3370 cm^{-1}.

The predominant formation of exhaustive alkylation product **III** and unsymmetrical dialkylation product **IV** may be explained by increase of NH acidity due to introduction of first 2-propynyl group which acts as electron acceptor. Product **III** is formed even when the reaction is carried out with equymolar amounts of the reactants.

It was quite reasonable to examine the possibility for alkylation of furazan **I** with less reactive alkyl halides, such as allyl bromide, ethyl bromide, and propyl bromide. In keeping with the data of [12], the reactivity ratio of allyl bromide, ethyl bromide, propyl bromide, and 2-propynyl bromide is 40:15:4:120 (in the alkylation of tertiary amines). Our results of alkylation of 3,4-diaminofurazan with the above reagents under conditions of phase-transfer catalysis were consistent with published data. In the reaction with allyl bromide the major product, tetraallyldiaminofurazan **V**, was isolated in 60% yield (reaction time 5 h). Tetraethyl- and tetrapropyldiaminofurazans **VI** and **VII** were obtained in 36 and 19% yield, respectively (Scheme 2). However, the rate of alkylation of 3,4-diaminofurazan (**I**) with ethyl and propyl bromides was considerably lower than with allyl and 2-propynyl bromides. Presumably, the presence of an electron-donor alkyl group on the nitrogen atom reduces the NH acidity, thus hampering the alkylation process.

Scheme 2.

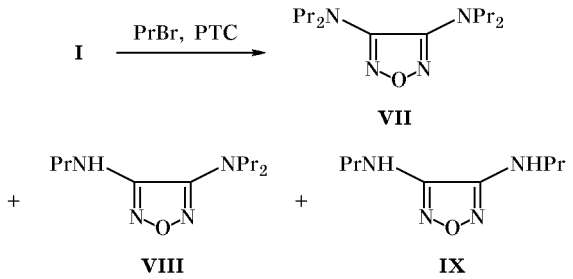


V, VI

V, R = $CH_2CH{=}CH_2$; **VI**, R = Et.

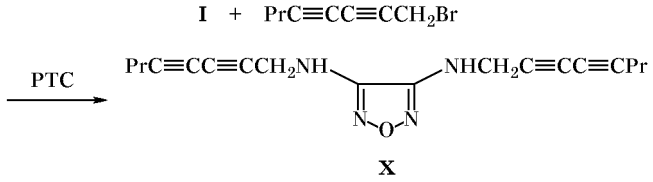
From the reaction mixture obtained in the alkylation of furazan **I** with propyl bromide we succeeded in isolating 7% of tripropyldiaminofurazan **VIII** and 12% of dipropyldiaminofurazan **IX** (Scheme 3). It should be noted that mono-, di-, and trialkyl derivatives were formed in all the above reactions, but in the other cases their amounts were insufficient for reliable identification.

Scheme 3.



With the goal of obtaining a furazan derivative having diacetylene substituent 3,4-diaminofurazan (**I**) was brought into reaction with 1-bromo-2,4-octadiyne. However, both alkylation products and initial bromide turned out to be unstable under the chosen conditions. The reaction was accompanied by strong tarring, and we succeeded in isolating only symmetrical disubstituted product **X** in ~5% yield (Scheme 4).

Scheme 4.



X

Our failure to obtain a compound combining a diacetylene system and a furazan ring in a high yield by alkylation of 3,4-diaminofurazan prompted us to explore another route, namely nucleophilic substitution in 3-amino-4-nitrofurazan (**II**) [7]. The nitro group in molecule **II** is a good leaving group in aromatic nucleophilic substitution reactions [13]. Mel'nikova *et al.* [14] previously reported on the reaction of 3-amino-4-nitrofurazan (**II**) with 2-azidoethanol in dimethylformamide (DMF), which resulted in formation of 3-(2-azidoethoxy)-4-aminofurazan.

Table 1. IR and ^1H and ^{13}C NMR spectra of furazan derivatives **III**–**XVII**

Comp. no.	IR spectrum,[a] ν, cm^{-1}	^1H NMR spectrum,[b] δ, ppm	^{13}C NMR spectrum,[b] δ_C, ppm
III	3300 (≡CH), 2150 (C≡C), 1630–1560 (C=NO), 1400–1370 (NO)	2.25 t (4H, C≡CH), 4.34 d (8H, CH_2)	38.91 (CH_2), 74.63, 77.87 (C≡C), 152.20 (C^3, C^4)
IV	3450, 3370 (NH_2), 3300 (≡CH), 2120 (C≡C), 1620, 1540 (C=NO), 1370 (NO)	2.39 t (2H, C≡CH), 3.13 d (4H, CH_2), 4.23 br.s (2H, NH_2)	38.92 (CH_2), 74.11 (C≡**C**H), 77.07 (**C**≡CH), 149.80 (**C**NCH_2), 151.56 (CNH_2)
V	3100, 1850 (=CH_2), 3040, 3000, 2940, 2870 (CH), 1650 (C=C), 1570 (C=NO), 1380 (NO)	3.85 d (8H, CH_2N), 5.25 m (8H, CH_2=C), 5.80 m (4H, C**H**=CH_2)	51.7 (CH_2N), 119.4, 133.0 (C=C), 153.6 (C^3, C^4)
VI	2960, 2870 (CH), 1570 (C=NO), 1390 (NO)	1.10 t (12H, CH_3), 3.26 q (8H, CH_2)	12.03 (CH_3), 43.50 (CH_2), 153.69 (C^3, C^4)
VII	2970–2850 (CH), 1570 (C=NO), 1390 (NO)	0.86 t (12H, CH_3), 1.56 m (8H, CH_2), 3.18 t (8H, CH_2N)	11.81 (CH_3), 20.10 (**C**H_2CH_3), 51.57 (NCH_2), 154.01 (C^3, C^4)
VIII	3410 (NH), 2970–2860 (CH), 1590 (C=NO), 1380 (NO)	0.90 t (6H, CH_3), 0.98 t (3H, CH_3), 1.58 m (4H, CH_2), 1.69 m (2H, CH_2), 3.13 t (4H, CH_2N), 3.25 q (2H, CH_2NH), 3.58 br.s (1H, NH)	11.74 (CH_3), 20.83 (NCH_2**C**H_2), 22.80 (NHCH_2**C**H_2), 47.07 (NHCH_2), 52.80 (NCH_2), 152.35 (C^3), 152.71 (C^4)
IX	3390 (NH), 2970–2870 (CH), 1590 (C=NO), 1390 (NO)	0.92 t (6H, CH_3), 1.65 m (4H, CH_2), 3.24 q (4H, CH_2N), 4.33 br.s (2H, NH)	11.71 (CH_3), 22.66 (**C**H_2CH_3), 46.98 (NCH_2), 150.59 (C^3, C^4)
X	3420 (NH), 2260 (C≡C), 1630–1570 (C=NO), 1370 (NO)	0.93 t (6H, CH_3), 1.62 m (4H, C**H**$_2CH_3$), 2.26 t (4H, C**H**$_2$Et), 4.03 br.s (2H, NH), 4.21 s (4H, NCH_2)	13.92 (CH_3), 21.81 (**C**H_2CH_3), 23.18 (**C**$H_2C_2H_5$), 61.13 (NCH_2), 65.42, 71.83, 72.01, 81.32 (C≡CC≡C), 151.07 (C^3, C^4)
XI	3400, 3330 (NH_2), 3310 (≡CH), 2200 (C≡C), 1630–1560 (C=NO), 1400–1370 (NO)	2.62 t (1H, C≡CH), 4.32 br.s (2H, NH_2), 4.95 d (2H, CH_2)	60.00 (CH_2), 76.68 (C≡**C**H), 77.60 (**C**≡CH), 148.03 (CNH_2), 157.01 (**C**OCH_2)
XII	3400, 3330 (NH_2), 1640–1570 (C=NO), 1380–1320 (NO)	4.84 br.s (4H, NH_2), 5.08 s (4H, CH_2)	59.66 (CH_2), 73.58 (C≡C), 149.18 (CNH_2), 157.57 (**C**OCH_2)
XIII	3510, 3410 (NH_2), 3320 (≡CH), 2130 (C≡C), 1630–1570 (C=NO), 1460, 1390 (NO)	2.05 s (1H, C≡CH), 2.74 t (2H, CH_2C≡C), 4.26 br.s (2H, NH_2), 4.42 t (2H, OCH_2)	19.51 (**C**H_2C≡C), 70.24 (OCH_2), 70.96 (C≡**C**H), 79.65 (**C**≡CH), 148.05 (CNH_2), 157.55 (**C**OCH_2)
XIV	3470, 3340 (NH_2), 2150 (C≡CC≡C), 1640, 1570 (C=NO), 1310 (NO), 1030 (CO)	2.03 m (4H, OCH_2C**H**$_2CH_2$), 2.52 t (4H, C**H**$_2$C≡C), 4.39 t (4H, OC**H**$_2$), 5.51 br.s (4H, NH_2)	15.41 (CH_2**C**H_2CH_2), 27.88 (**C**H_2C≡C), 66.05 (C≡**C**C≡C), 70.77 (O**C**H_2), 76.75 (**C**≡CC≡**C**), 149.02 (CNH_2), 158.14 (**C**OCH_2)
XV	3480, 3340 (NH_2), 2150 (C≡CC≡C), 1640, 1570 (C=NO), 1320 (NO), 1040 (CO)	1.70 m (2H, C**H**$_2CH_2OH$), 2.04 m (2H, OCH_2C**H**$_2$), 2.36 t (2H, C**H**$_2CH_2CH_2OH$), 2.51 t (2H, OCH_2CH_2C**H**$_2$), 3.60 m (2H, C**H**$_2$OH), 3.72 t (1H, OH), 4.42 t (2H, OC**H**$_2$), 5.50 br.s (2H, NH_2)	15.43 (OCH_2**C**H_2CH_2), 27.94 (OCH_2CH_2**C**H_2), 30.14 (CH_2-**C**H_2CH_2OH), 31.76 (**C**H_2CH_2-CH_2OH), 60.38 (**C**H_2OH), 70.78 (O**C**H_2), 65.39, 66.31, 76.18, 77.98 (C≡CC≡C), 149.02 (CNH_2), 158.14 (**C**OCH_2)

Table 1. (Contd.)

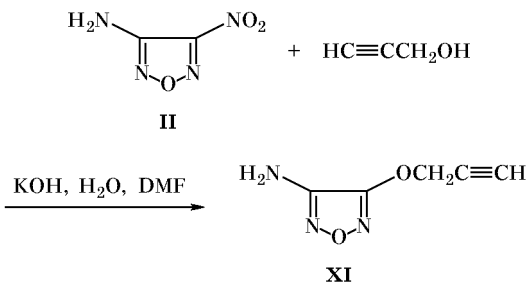
Comp. no.	IR spectrum,[a] ν, cm^{-1}	^1H NMR spectrum,[b] δ, ppm	^{13}C NMR spectrum,[b] δ_C, ppm
XVI	3470, 3320 (NH_2), 2160 (C≡CC≡C), 1640, 1570 (C=NO), 1310 (NO), 1060 (CO)	2.48 t (2H, C**H**$_2$CH$_2$OH), 2.89 t (2H, OCH$_2$C**H**$_2$), 3.68 m (2H, C**H**$_2$OH), 4.11 t (1H, OH), 4.45 t (2H, OCH_2), 5.52 br.s (2H, NH_2)	19.68 (**C**H$_2$CH$_2$OH), 23.45 (OCH$_2$-**C**H$_2$), 60.40 (**C**H$_2$OH), 69.92 (O**C**H$_2$), 66.00, 67.04, 73.26, 76.46 (C≡**C**C≡C), 148.95 (CNH_2), 157.93 (**C**OCH$_2$)
XVII	3630 (OH), 2250 (C≡CC≡C), 1640, 1600 (C=C), 1040 (CO)	2.13 br.s (1H, OH), 2.62 t (2H, C**H**$_2$CH$_2$OH), 3.80 t (2H, C**H**$_2$-OH), 5.65 m (1H, CH_2=C**H**), 5.80 m (2H, C**H**$_2$=CH)	24.31 (**C**H$_2$CH$_2$OH), 61.11 (**C**H$_2$-OH), 67.04, 74.62, 74.95, 81.43 (C≡**C**C≡C), 116.47 (**C**H$_2$=CH), 130.63 (CH_2=**C**H)

[a] The IR spectra of compounds **III** and **V**–**X** were recorded in CCl_4, of **IV**, **XI**, **XIII**, and **XVII**, in $CHCl_3$, and of **XII** and **XIV**–**XVI**, in KBr.

[b] The NMR spectra of compounds **XIV**–**XVI** were measured in acetone-d_6, the ^1H and ^{13}C NMR spectra of **XII** were recorded in CD_3CN and THF-d_8, respectively, and the NMR spectra of the other compounds were obtained in $CDCl_3$.

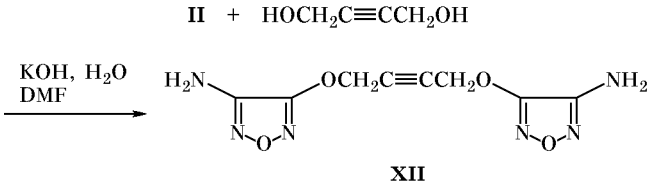
The corresponding carbanion was generated by the action of 45% KOH at 20°C. We have found that furazan **II** reacts with acetylenic alcohols even at 2°C to afford the corresponding alkynyl ethers. By the reaction of **II** with 2-propynyl alcohol we obtained 3-amino-4-(2-propynyloxy)furazan (**XI**) in 43% yield (Scheme 5).

Scheme 5.



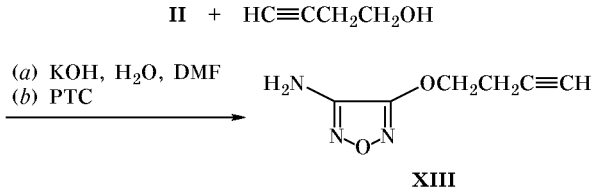
1,4-Bis(4-amino-1,2,5-oxadiazol-3-yloxy)-2-butyne (**XII**) was isolated in 68% yield in the reaction of furazan **II** with 2-butyne-1,4-diol (Scheme 6).

Scheme 6.



However, reactions of **II** with diacetylenic diols, such as 2,4-hexadiyne-1,6-diol and 3,5-octadiyne-1,8-diol, resulted in strong tarring of the mixture, and no individual product was isolated. Therefore, we tried to carry out these reactions under milder conditions, resorting to phase-transfer catalysis. For this purpose, 3-amino-4-nitrofurazan was brought into reaction with 3-butyn-1-ol according to the procedure reported in [14] (method *a*) and under conditions of phase-transfer catalysis (method *b*). In the first case we isolated 3-amino-4-(3-butynyloxy)furazan (**XIII**) in 40% yield. The same product was obtained by method *b*, but the yield of **XIII** increased to 53% (Scheme 7).

Scheme 7.



These results showed that nucleophilic substitution of the nitro group in 3-amino-4-nitrofurazan by monoacetylenic alcohols is successful both under usual conditions and in the presence of phase-transfer catalyst. However, the reaction of **II** with diacetylenic diols occurs only under phase-transfer catalysis. In order to obtain dialkynyl derivatives of furazan we also used 2,4-hexadiyne-1,6-diol, 3,5-octadiyne-1,8-diol, and 4,6-decadiyne-1,10-diol. Our experimental data revealed a relation between the stability of diacetylenic furazan derivatives and the number of methylene units therein. Target products **XIV** and **XV**

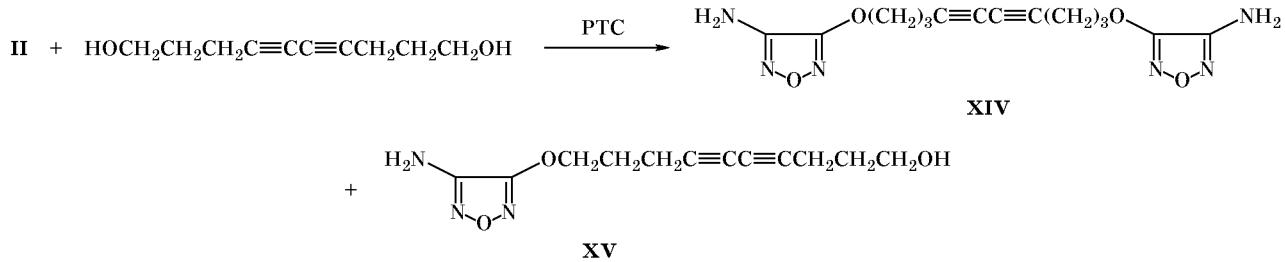
Table 2. Yields, melting points or refractive indices, and elemental analyses of furazan derivatives **III**–**XVII**

Comp. no.	Yield, %	mp, °C (n_D)[a]	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
III	50	79–80	66.32	4.69	22.19	$C_{14}H_{12}N_4O$	66.65	4.75	22.21
IV	11	97–98	55.13	4.60	31.53	$C_8H_8N_4O$	54.54	4.58	31.80
V	60	$(1.5050)^{18}$	65.09	7.54	21.44	$C_{14}H_{20}N_4O$	64.59	7.74	21.52
VI	36	$(1.4709)^{22}$	56.80	9.18	25.87	$C_{10}H_{10}N_4O$	56.58	9.50	26.39
VII	19	$(1.4695)^{17}$	62.60	10.32	20.18	$C_{14}H_{28}N_4O$	62.65	10.52	20.87
VIII	12	$(1.4814)^{17}$	58.84	9.96	24.11	$C_{11}H_{22}N_4O$	58.38	9.80	24.76
IX	7	$(1.4978)^{17}$	51.91	8.39	28.67	$C_8H_{16}N_4O$	52.15	8.75	30.41
X	5	76–78	70.10	6.53	17.87	$C_{18}H_{20}N_4O$	70.10	6.53	18.17
XI	43	65–66	43.01	3.80	29.85	$C_5H_5N_3O_2$	43.16	3.62	30.21
XII	68	160–161	38.01	3.39	33.17	$C_8H_8N_6O_4$	38.10	3.20	33.32
XIII	40, 53[b]	66–68	47.49	4.70	27.46	$C_6H_7N_3O_2$	47.06	4.61	27.44
XIV	23	156–160	50.68	4.80	24.10	$C_{14}H_{16}N_6O_4$	50.60	4.85	25.29
XV	10	63–67	57.67	6.09	16.86	$C_{12}H_{15}N_3O_3$	57.82	6.07	16.86
XVI	10	65–67	54.26	5.16	17.94	$C_{10}H_{11}N_3O_3$	54.30	5.01	19.00
XVII	10	Oily substance	79.65	6.53	–	C_8H_8O	79.97	6.71	–

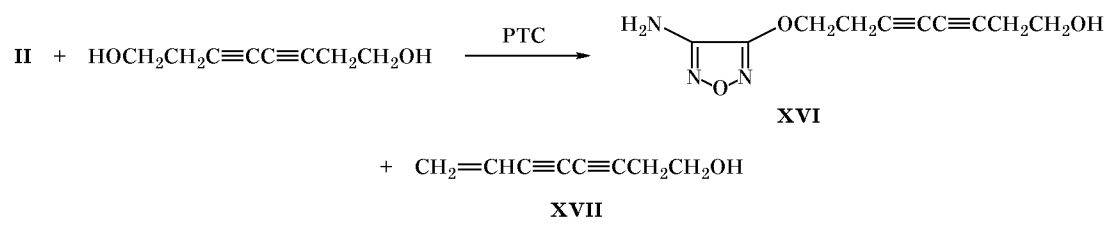
[a] The superscript denotes the temperature at which the refractive index was measured.
[b] According to methods *a* and *b*, respectively (see Experimental).

were isolated in 23 and 10% yield, respectively, only in the reaction of **II** with 4,6-decadiyne-1,10-diol (Scheme 8). The reaction of 3-amino-4-nitrofurazan (**II**) with 3,5-octadiyne-1,8-diol gave only monosubstituted product, furazan **XVI**, in 10% yield. 7-Octene-3,5-diyn-1-ol (**XVII**) was isolated as by-product (Scheme 9). By special experiment we showed that compound **XVII** is formed by decomposition of **XVI**: When 3,5-octadiyne-1,8-diol was kept for 2 days under the same conditions but in the absence of 3-amino-4-nitrofurazan, the reaction mixture remained unchanged. The reaction of **II** with 2,4-hexadiyne-1,6-diol both in the system KOH–H_2O–DMF and under PTC conditions was accompanied by strong tarring, and no nucleophilic substitution products were isolated.

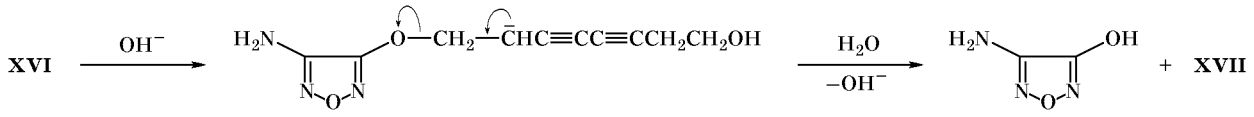
Scheme 8.



Scheme 9.

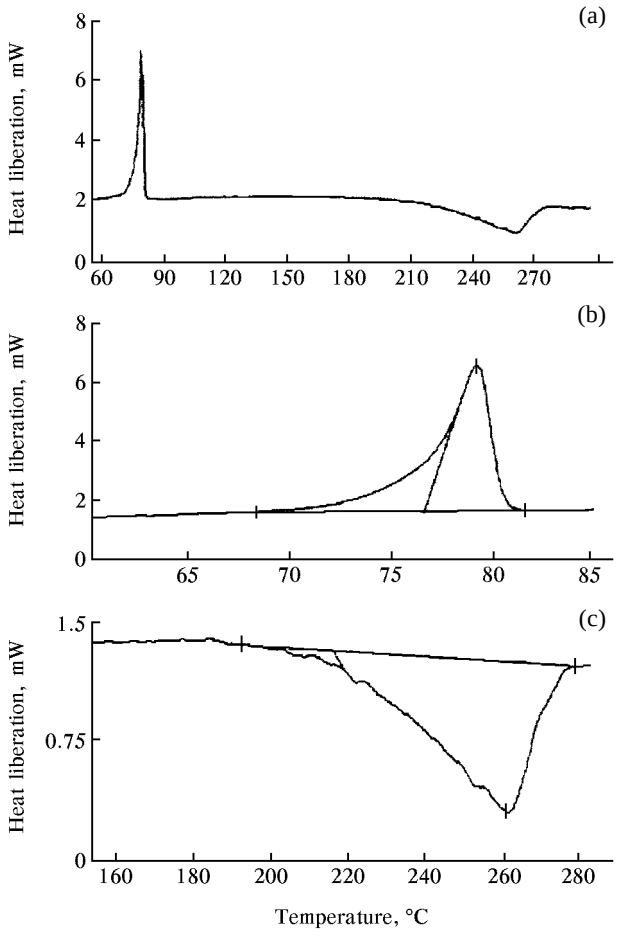


Scheme 10.



The difference in the behavior of mono- and diacetylenic compounds in the alkylation of diamine **I** and nucleophilic substitution of the nitro group in **II** may be explained by increase in CH acidity of the methylene group adjacent to the C≡C bond. Its CH acidity is greater in compounds containing a system of two conjugated triple bonds [15–18]. This factor, together with the electron-acceptor effect of the furazan ring, is responsible for the observed decomposition of compound **XVI**. A probable mechanism of this process is shown in Scheme 10.

Some words should be said about specific features of the mass spectra of furazan-containing acetylenes and diacetylenes. The presence in the mass spectra of molecular ion peaks can be regarded as an additional proof for the proposed structure of the products. The spectrum of compound **III** contains the following ion peaks, *m*/*z*: 253 $[M+1]^+$, 213 $[M-CH_2C{\equiv}CH]^+$, 174 $[M-2CH_2C{\equiv}CH]^{+\cdot}$, 79 $[HC{\equiv}CCH_2NCN]^+$, 65 $[HC{\equiv}CCH_2NC]^+$. However, fragmentation pathways typical of furazans with fairly simple substituents in the ring (like compound **III**) are not seen so clearly in the mass spectra of diacetylenic derivatives **XIV**–**XVI**. This is the result of the presence of two triple bonds in their molecules. The degree of unsaturation of the aliphatic moieties in the diacetylenic derivatives is equal to 4, as in benzene and other aromatic compounds. Due to ready migration of multiple bonds along the carbon chain in ionized molecules and high probability of cyclization processes [19] the most abundant ions in the mass spectra of diacetylenic furazan compounds are those typical of benzene derivatives, *m*/*z*: 147 $[C_{11}H_{15}]^+$, 115 $[C_9H_7]^{+\cdot}$, 102 $[C_8H_6]^+$, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 65 $[C_5H_5]^+$, 51 $[C_4H_3]^+$, 39 $[C_3H_3]^+$.



Differential scanning calorimetry data for *N*,*N*,*N*′,*N*′-tetrakis(2-propynyl)-3,4-diaminofurazan (**III**).

Furazan-containing diacetylenes **X** and **XIV**–**XVI** are potential monomers for solid-phase topochemical polymerization, i.e., a single crystal of diacetylenic monomer could give rise to a single crystal of polydiacetylene, which is characterized by highly ordered structure. Solid-phase topochemical polymerization occurs as poly-1,4-addition; it can be initiated by heating and UV or γ-irradiation. The products are quasiunidimensional molecules having a conjugated framework with either enyne or butatriene (cumulene) structure, the former usually prevailing [20]. The transformation of diacetylene into polydiacetylene is accompanied by appearance of an intense color due to polymeric chains in the crystal matrix of diacetylene. The rate of solid-phase topochemical polymerization and the yield of polydiacetylene depend very strongly on the monomer structure which is responsible for favorable packing of diacetylene molecules in the crystallographic unit cell.

The mechanism of formation, properties, and application of polydiacetylenes were summarized in [21–23]. The most interesting are nonlinear optical properties of polymeric diacetylenes. Among all organic compounds, polydiacetylenes are characterized by the greatest values of the third-order nonlinear optical susceptibility [24]. In the series of furazan-

containing diacetylenes synthesized in the present work, compound **XV** turned out to be active under scattered daylight: it acquired a blue color during isolation.

Thermochemical properties of our products must also be considered. Tetra(2-propynyl)diaminofurazan **III** was studied by differential scanning calorimetry (DSC; see figure). The measurements were carried out in a cell filled with argon. Curve (a) shows thermal effects observed on heating of a sample of furazan **III** to 300°C. The endothermic effect at 79.38°C (184.57 J/g) results from melting of the substance. As follows from plot (b), this process is accompanied by an additional effect which appears as a shoulder on the main peak. In the temperature range from 192.22 to 279.18°C (c) an exothermic effect is observed (–198.36 J/g) with its maximum at 261.85°C; presumably, it reflects decomposition of the sample. After heating to 300°C, 84.5% of the sample weight is lost.

We also calculated the enthalpy of formation ΔH_f of compound **III**, following the procedure developed by Avakyan [25]. The calculated value of ΔH_f is 299 kcal/mol. For comparison, the corresponding parameter of compound **XIV** is 48.2 kcal/mol. Thus furazan **III** possesses a much higher internal energy than **XIV** due to the presence of greater number of triple bonds in the molecule.

EXPERIMENTAL

The IR spectra were measured from 5% solutions of compounds in $CHCl_3$ or CCl_4 or from samples pelleted with KBr using a Specord 75IR instrument. The UV spectra were recorded on an SF-26 spectrophotometer in acetonitrile. The ^1H and ^{13}C NMR spectra were obtained on a Buker DPX-300 spectrometer (300 MHz for ^1H) using $CDCl_3$, CD_3COCD_3, and CD_3CN as solvents. The mass spectra were run on an MKh-1330 GC–MS system (energy of ionizing electrons 70 eV). The data of differential scanning calorimetry were obtained with the aid of a Perkin–Elmer DSC-7 instrument. Thin-layer chromatography was performed on Silufol UV-254 plates; spots were visualized by UV irradiation or by treatment with iodine vapor or a solution of potassium permanganate.

Initial 3,4-diaminofurazan (**I**) and 3-amino-4-nitrofurazan (**II**) were synthesized by the procedures described in [6, 7]. The spectral and analytical data of the newly synthesized compounds are collected in Tables 1 and 2.

***N,N,N′,N′*-Tetrakis(2-propynyl)-3,4-diaminofurazan (III) and *N,N*-bis(2-propynyl)-3,4-diaminofurazan (IV).** To a solution of 0.5 g (5 mmol) of furazan **I** in 15 ml of anhydrous tetrahydrofuran we added 2.76 g (20 mmol) of anhydrous K_2CO_3, 1.21 g (20 mmol) of powdered KOH, and a catalytic amount of tetrabutylammonium iodide. A solution of 2 ml (27 mmol) of 2-propynyl alcohol in 5 ml of anhydrous THF was added with stirring, and the mixture was stirred until initial furazan **I** disappeared (TLC). The mixture was filtered, and the precipitate was washed with diethyl ether. The filtrate was washed with water until neutral reaction and was dried over $MgSO_4$. The products were isolated by preparative thin-layer chromatography on silica gel using hexane–ether (1 : 1) as eluent. Compound **III**: UV spectrum (CH_3CN), λ_{max}, nm (ε): 254 (460). Mass spectrum, *m*/*z*: 253 $[M+1]^+$, 213 $[M-CH_2C{\equiv}CH]^{+\cdot}$, 174 $[M-2CH_2C{\equiv}CH]^+$, 79 $[HC{\equiv}CCH_2NCN]^+$, 65 $[HC{\equiv}CCH_2NC]^+$. Also, 0.1 g (11%) of product **IV** was isolated.

***N,N,N′,N′*-Tetraallyl-3,4-diaminofurazan (V)** was synthesized in a similar way from 0.3 g (3 mmol) of furazan **I** and 1 ml (12 mmol) of allyl bromide. Mass spectrum, *m*/*z* (I_{rel}, %): 260 (2) $[M]^{+\cdot}$, 259 (7) $[M-H]^+$, 231 (19), 219 (28) $[M-CH_2CH{=}CH_2]^+$, 218 (36) $[M-H-CH_2CH{=}CH_2]^{+\cdot}$, 204 (15), 188 (19), 177 (15) $[M-2CH_2CH{=}CH_2]^+$, 163 (13), 148 (100), 123 (49), 121 (38), 108 (19), 96 (23), 93 (21), 81 (45) $[H_2C{=}CHCH_2NCN]^+$, 67 (40) $[H_2C{=}CHCH_2NC]^+$, 56 (23).

***N,N,N′,N′*-Tetraethyl-3,4-diaminofurazan (VI)** was synthesized as described above for compound **III** from 0.3 g (3 mmol) of furazan **I** and 1.34 ml (18 mmol) of ethyl bromide.

***N,N,N′,N′*-Tetrapropyl-3,4-diaminofurazan (VII), *N,N,N′*-tripropyl-3,4-diaminofurazan (VIII), and *N,N′*-dipropyl-3,4-diaminofurazan (IX)** were obtained as described above for compound **III** from 0.3 g (3 mmol) of furazan **I** and 1.64 ml (18 mmol) of propyl bromide.

***N,N′*-Bis(2,4-octadiynyl)-3,4-diaminofurazan (X)** was synthesized as described above for compound **III** from 0.3 g (3 mmol) of furazan **I** and 2.22 g (12 mmol) of 1-bromo-2,4-octadiyne. The reaction was assumed to be complete when the initial bromodiacetylene disappeared (TLC).

3-Amino-4-(2-propynyloxy)furazan (XI) was prepared by the procedure described in [14] from 0.13 g (1 mmol) of furazan **II** and 0.09 ml (1.5 mmol) of 2-propynyl alcohol on cooling to 2°C.

1,4-Bis(4-amino-1,2,5-oxadiazol-3-yloxy)-2-butyne (XII) was synthesized by the procedure described in [14] from 0.16 g (1.2 mmol) of furazan **II** and 0.05 g (0.6 mmol) of 2-butyne-1,4-diol.

3-Amino-4-(3-butynyloxy)furazan (XIII). *a.* The procedure was similar to that described in [14]; 0.13 g (1 mmol) of furazan **II** and 0.11 ml (1.5 mmol) of 3-butyn-1-ol were taken.

b. A mixture of 0.12 g (2.1 mmol) of powdered potassium hydroxide, 0.29 g (2.1 mmol) of anhydrous potassium carbonate, and a catalytic amount of tetrabutylammonium iodide was added to a solution of 0.13 g (1 mmol) of furazan **II** and 0.11 ml (1.5 mmol) of 3-butyn-1-ol in 5 ml of DMF. The progress of the reaction was monitored by TLC. When initial furazan **II** disappeared, the mixture was poured into 50 ml of cold water and was treated with diethyl ether. The extract was washed with water until neutral washings and dried over $MgSO_4$. The product was isolated as in the preceding experiment.

1,10-Bis(4-amino-1,2,5-oxadiazol-3-yloxy)-4,6-decadiyne (XIV) and 10-(4-amino-1,2,5-oxadiazol-3-yloxy)-4,6-decadiyn-1-ol (XV). A mixture of 0.18 g (3.2 mmol) of powdered potassium hydroxide, 0.44 g (3.2 mmol) of anhydrous K_2CO_3, and a catalytic amount of tetrabutylammonium iodide was added to a solution of 0.42 g (3.2 mmol) of furazan **II** and 0.26 g (1.6 mmol) of 4,6-decadiyn-1,10-diol in 15 ml of THF, cooled to 2°C. The progress of the reaction was monitored by TLC. After 2 h, the precipitate was filtered off and washed with diethyl ether. The organic phase was washed with water until neutral washings and dried over $MgSO_4$. The solvent was distilled off, and a light brown solid precipitated during this process. The precipitate was washed with a small amount of ether and dried. UV spectrum (CH_3CN), λ_{max}, nm (ε): 240 (1140). Mass spectrum, *m*/*z* (I_{rel}, %): 332 (1) $[M]^{+\cdot}$, 315 (1), 302 (14) $[M-NO]^{+\cdot}$, 213 (4), 202 (10), 189 (20), 174 (18), 147 (16), 128 (16), 115 (39), 104 (43), 103 (45), 93 (8), 91 (69), 77 (100), 65 (84), 51 (34), 43 (39), 42 (24) $[H_2NC{\equiv}N]^{+\cdot}$, 41 (31), 39 (14). Furazan **XV** was isolated by preparative TLC on silica gel (eluent ether) from the product mixture obtained after removal of ether. UV spectrum (CH_3CN), λ_{max}, nm (ε): 240 (470). Mass spectrum, *m*/*z* (I_{rel}, %): 249 (2) $[M]^{+\cdot}$, 232 (2), 219 (3) $[M-NO]^{+\cdot}$, 204 (3), 193 (12), 191 (8), 176 (5), 174 (4), 163 (11), 149 (23), 128 (10), 121 (18), 115 (26), 103 (31), 91 (85), 77 (100), 65 (38), 51 (36), 43 (23), 42 (18) $[H_2NC{\equiv}N]^{+\cdot}$.

8-(4-Amino-1,2,5-oxadiazol-3-yloxy)-3,5-octadiyn-1-ol (XVI). A mixture of 0.3 g (5.2 mmol) of powdered KOH, 0.72 g (5.2 mmol) of anhydrous K_2CO_3, and a catalytic amount of tetrabutylammonium iodide was added to a solution of 0.34 g (2.6 mmol) of furazan **II** and 0.25 g (1.8 mmol) of 3,5-octadiyne-1,8-diol in 10 ml of THF, cooled to 3°C. The progress of the reaction was monitored by TLC. After 30 min, the precipitate was filtered off and washed with diethyl ether. The organic phase was washed with water until neutral washings and dried over $MgSO_4$. The solvent was removed, and the products were isolated from the residue by preparative thin-layer chromatography on silica gel using ether–hexane (5 : 1) as eluent. Compound **XVI**: UV spectrum (CH_3CN), λ_{max}, nm (ε): 237 (570). Mass spectrum, *m*/*z* (I_{rel}, %): 221 (1) $[M]^{+\cdot}$, 191 (9) $[M-NO]^{+\cdot}$, 173 (2), 161 (3), 149 (2), 133 (3), 121 (22), 103 (9), 93 (36), 92 (25), 91 (57), 77 (100), 69 (14), 65 (48), 63 (32), 51 (32), 39 (27). Also, 7-octene-3,5-diyn-1-ol (**XVII**) was isolated, which was formed by decomposition of furazan **XVI**.

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REFERENCES

1. Dielimoriba, D., Berezina, S.E., Remizova, L.A., and Domnin, I.N., *Vestn. S.-Peterb. Gos. Univ., Ser. 4*, 1999, no. 4, pp. 98–104.
2. Berezina, S.E., Remizova, L.A., and Domnin, I.N., *Book of Abstracts of Int. Conf. "Reaction Mechanisms and Organic Intermediates,"* St. Petersburg, 2001, pp. 85–86.
3. Temkin, O.N., Shestakov, T.K., and Treger, Yu.A., *Atsetilen. Khimiya. Mekhanizmy reaktsii. Tekhnologiya* (Acetylene: Chemistry, Reaction Mechanisms, and Technology), Moscow: Khimiya, 1991.
4. Friedrichsen, W., *Houben–Weyl. Methoden der organischen Chemie*, Schaumann, E., Ed., Stuttgart: Georg Thieme, 1994, vol. E8c, part 3, pp. 648–696.
5. Paton, R.M., *Comprehensive Heterocyclic Chemistry II*, Katritzky, A.R., Rees, C.W., and Scriven, E.F.V., Eds., Oxford: Pergamon, 1996, vol. 4, pp. 229–365.
6. Gunasecaran, A., Jayachandran, T., Boyer, J.H., and Trudell, M.L., *J. Heterocycl. Chem.*, 1995, vol. 32, no. 4, pp. 1405–1407.
7. Solodyuk, G.D., Boldyrev, M.D., and Gidaspov, B.V., *Zh. Org. Khim.*, 1981, vol. 17, no. 4, pp. 861–862.
8. Andrianov, V.G. and Eremeev, A.V., *Khim. Geterotsikl. Soedin.*, 1984, no. 9, pp. 1155–1170.
9. Pozharskii, A.F., Zvezdina, E.A., Kashparov, I.S., Andreichikov, Yu.P., Mr'yanovskii, V.M., and Simonov, A.M., *Khim. Geterotsikl. Soedin.*, 1971, no. 9, pp. 1230–1237.

10. Corbel, B., Paugam, J.P., Dreux, M., and Savignac, P., *Tetrahedron Lett.*, 1976, no. 11, pp. 835–838.
11. Mostamandi, A., Remizova, L.A., Fomenkova, T.N., and Favorskaya, I.A., *Zh. Org. Khim.*, 1982, vol. 18, no. 5, pp. 977–980.
12. Ermilova, E.V., *Cand. Sci. (Chem.) Dissertation*, Leningrad, 1975.
13. Pozharskii, A.F., *Teoreticheskie osnovy khimii geterotsiklov* (Theoretical Foundations of the Chemistry of Heterocyclic Compounds), Moscow: Khimiya, 1985, pp. 209–267; Sheremetev, A.B., *Ros. Khim. Zh.*, 1997, no. 1, pp. 43–54.
14. Mel'nikova, S.F., Pirogov, S.V., Vergizov, S.N., and Tselinskii, I.V., *Russ. J. Org. Chem.*, 1999, vol. 35, no. 1, pp. 137–140.
15. Klein, J. and Becker, J.J., *J. Chem. Soc., Perkin Trans. 2*, 1973, no. 5, pp. 599–603.
16. Remizova, L.A., Balova, I.A., and Favorskaya, I.A., *Zh. Org. Khim.*, 1986, vol. 22, no. 11, pp. 2459–2460.
17. Balova, I.A., Remizova, L.A., and Favorskaya, I.A., *Zh. Org. Khim.*, 1990, vol. 26, no. 4, pp. 729–731.
18. Balova, I.A., Zakharova, I.V., and Remizova, L.A., *Zh. Org. Khim.*, 1993, vol. 29, no. 9, pp. 1732–1738.
19. Takhistov, V.V., *Organicheskaya mass-spektrometriya* (Organic Mass Spectrometry), Leningrad: Nauka, 1990.
20. Shklover, V.E., Timofeeva, T.V., and Struchkov, Yu.T., *Usp. Khim.*, 1986, vol. 55, no. 8, pp. 1282–1318.
21. Vinogradov, G.A., *Usp. Khim.*, 1984, vol. 53, no. 1, pp. 135–175.
22. Misin, V.M. and Cherkashin, M.I., *Usp. Khim.*, 1985, vol. 54, no. 6, pp. 956–1008.
23. *Polydiacetylenes. Synthesis, Structure and Electronic Properties*, Bloor, D. and Chance, R.R., Eds., Dordrecht: Nijhoff, 1985.
24. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Chemla, D.S. and Zyss, J., Eds., Orlando: Academic, 1987. Translated under the title *Nelineinye opticheskie svoistva organicheskikh molekul i kristallov*, Moscow: Mir, 1989, vol. 2, pp. 5–128.
25. Avakyan, G.A., *Raschet energeticheskikh i vzryvchatykh kharakteristik vzryvchatykh veshchestv* (Calculation of the Energy and Explosion Parameters of Explosives), Moscow: Dzerzhinskii Military Engineering Academy, 1964.