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# Three-Component Synthesis of 2-(4-Amino-2,5-dihydro-1*H*-imidazol-5-ylidene)malononitriles

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**Abstract**—2-(4-Amino-2,5-dihydro-1*H*-imidazol-4-ylidene)malononitriles were synthesized by three-component reaction of tetracyanoethylene, carbonyl compound, and ammonium acetate. The synthesis can be performed in two steps with intermediate isolation of 2-aminoethene-1,1,2-tricarbonitrile, as well as using preliminarily prepared 2-aminoethene-1,1,2-tricarbonitrile and 1,3,5-trisubstituted 2,4-diazapentadienes.

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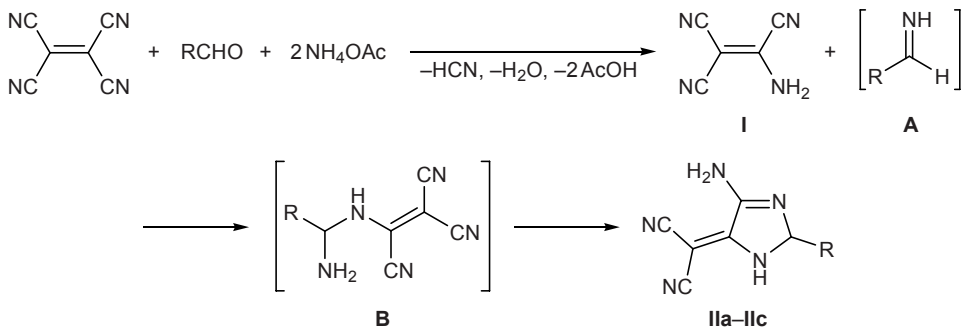
Reactions of tetracyanoethylene with ketones underlie many syntheses of aliphatic, alicyclic, and heterocyclic compounds that are difficult to obtain by other methods [1–5]. Despite considerable progress in studying the chemistry of 4-oxoalkane-1,1,2,2-tetracarbonitriles (tetracyanoethylene adducts with ketones), analogous reactions with aldehydes were not reported. Presumably, the reason is that tetracyanoalkanals are difficult to isolate under the classical reaction conditions due to their high reactivity. Therefore, we presumed that three-component transformations are feasible. Such reactions ensure self-assembly of heterocyclic or alicyclic systems from simple precursors via one-pot processes [6]. Following this approach, we succeeded in effecting three-component reactions of tetracyanoethylene with aldehydes and obtaining substituted 6-imino-2,7-dioxabicyclo[3.2.1]octane-4,4,5-tricarbonitriles [7], 5,5-dialkyl-2-halo-6-hydroxy-5,6-dihydro-1*H*-pyridine-3,4,4-tricarbonitriles [8], and 2,4-dialkyl-7-imino-6-oxabicyclo[3.2.1]oct-3-ene-1,8,8-tricarbonitriles [9].

While continuing systematic studies on reactions of tetracyanoethylene with aldehydes, we have found that these compounds in the presence of ammonium acetate (as source of ammonia) give rise to substituted 2-(4-amino-2-alkyl-2,5-dihydro-1*H*-imidazol-5-ylidene)malononitriles **IIa**–**IIc** in 36–42% yield (Scheme 1). The reaction sequence is likely to include initial formation of aminotricyanoethylene **I** and aldehyde imine **A**. It is known that tetracyanoethylene having an electron-deficient double bond readily reacts with electron-rich compounds [10]. An example is its

**Scheme 1.**




R = *i*-Pr (**a**), $Et_2CH$ (**b**), BuEtCH (**c**).

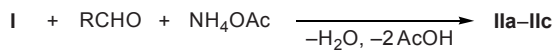
reaction with amines, which leads to R-aminotricyanoethylenes [10, 11]. The reaction of tetracyanoethylene with ammonia gives no analogous derivative, but the subsequent transformations result in the formation of 2-(1,2,2-tricyanovinylamino)ethene-1,1,2-tricarbonitrile ammonium salt [10, 12].

The use of ammonium acetate allowed us to avoid reactions originating from basic properties of the reagent. Acetic acid and hydrogen cyanide accumulating in the reaction mixture should stabilize enamino nitrile **I** formed in the first stage even more strongly. To verify this assumption, we examined the reaction of tetracyanoethylene with excess ammonium acetate in dioxane. As a result, we isolated 94% of 2-aminoethene-1,1,2-tricarbonitrile (**I**) whose structure was proved by X-ray analysis (Fig. 1).

The formation of aminoethenetricarbonitrile **I** by reaction of tetracyanoethylene with ammonium acetate is likely to be accompanied by transformation of aldehydes into imines **A**. The latter are very unstable, for they readily undergo hydrolysis or polymerization, and they react *in statu nascendi* with vinylamine **I** to form intermediate **B**. The amino group in the latter is involved in intramolecular cyclization with participation of the neighboring cyano group, yielding final imidazole derivatives **II** (Scheme 1).

To verify the proposed scheme of transformations, we performed reaction of aminoethenetricarbonitrile **I** with aldehydes in the presence of ammonium acetate. In fact, the products were 2-(4-amino-2-alkyl-2,5-dihydro-1*H*-imidazol-5-ylidene)malononitriles **IIa**–**IIc** (42–56%; Scheme 2). These data confirmed formation of aminoethenetricarbonitrile **I** in the first stage.

**Scheme 2.**




In order to refine the scheme of formation of compounds **IIa**–**IIc**, we performed additional experiments in which aminotricyanoethylene **I** was brought into reactions with preliminarily prepared imines **A**. Taking into account the above stated instability of aldehyde imines (which cannot be isolated as individual substances), the reactions were carried out with their structural analogs, 1,3,5-trisubstituted 2,4-diazapenta-1,4-dienes **IIIa**–**IIId**. By reactions of compounds **IIIa**–**IIId** with aminoethenetricarbonitrile **I** we also obtained imidazolylidenemalononitriles **IIa**–**IId** (Scheme 3). These reactions occurred at a higher rate, and the yields of compounds **II** were greater (55–63%)

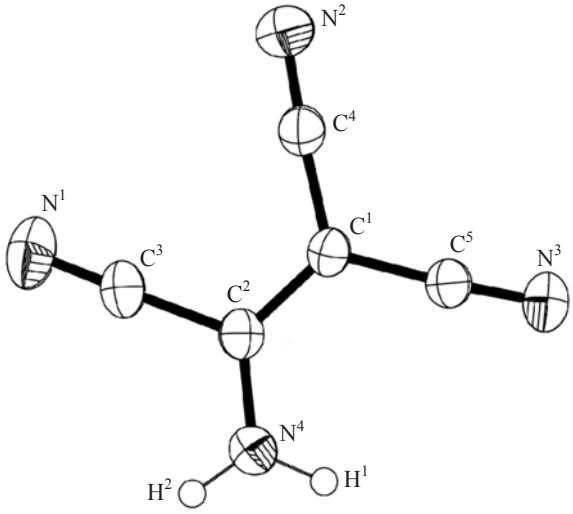



**Fig. 1.** Structure of the molecule of 2-aminoethene-1,1,2-tricarbonitrile (**I**) according to the X-ray diffraction data.

than in the reactions shown in Schemes 1 and 2. We thus succeeded in reacting aminoethenetricarbonitrile **I** with hydrobenzamide (**IIId**) as synthetic equivalent of benzaldehyde imine.

We proposed two schemes to rationalize the observed transformations. According to the first of these, the process begins with addition of the amino group in aminoethenetricarbonitrile **I** at the C=N bond of compounds **III**. This scheme is analogous to the reaction of **I** with carbonyl compounds in the presence of ammonium acetate (Scheme 1). The second path is shown in Scheme 3. In this case, nucleophilic nitrogen atom in Schiff base **III** attacks electrophilic carbon atom of the cyano group in **I**, and next follows imidazole ring closure. Presumably, the reactions following these schemes are characterized by different rates, depending on steric factors related to the substituents.

The revealed reaction of tetracyanoethylene with aldehydes, leading to imidazole derivatives **IIa**–**IId**,

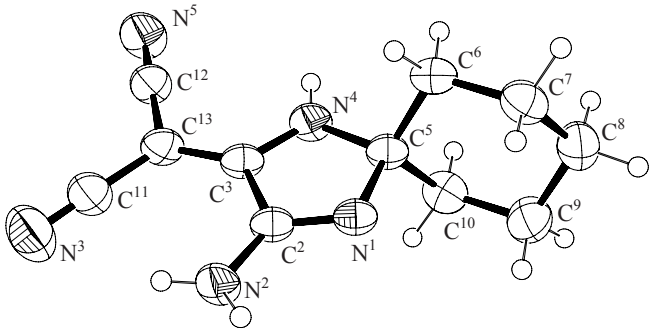
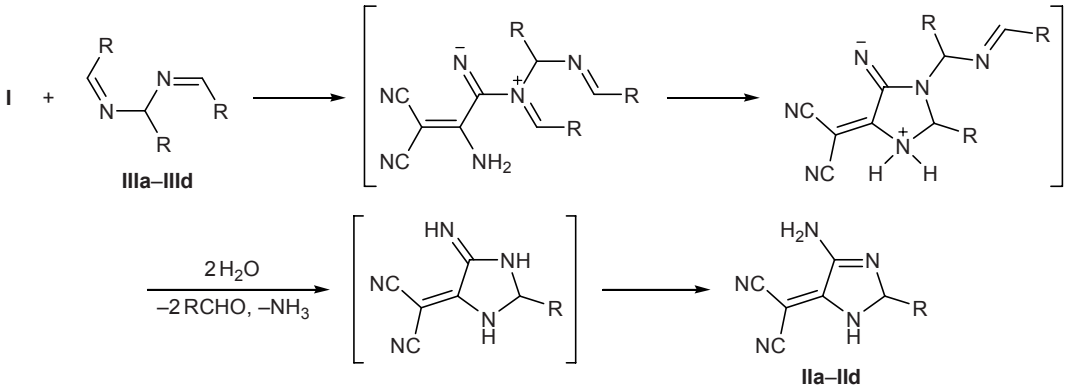


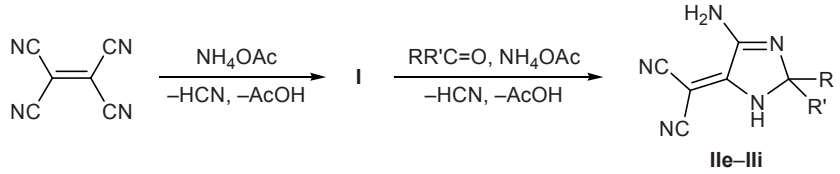

**Fig. 2.** Structure of the molecule of 2-(3-amino-1,4-diazaspiro[4.5]dec-3-en-2-ylidene)malononitrile (**IIe**) according to the X-ray diffraction data.

**Scheme 3.**




R = *i*-Pr (**a**), $Et_2CH$ (**b**), BuEtCH (**c**), Ph (**d**).

**Scheme 4.**




RR′ = $(CH_2)_5$ (**e**), $(CH_2)_2CH(Me)(CH_2)_2$ (**f**), $(CH_2)_2CH(Ph)(CH_2)_2$ (**g**), $CH(Me)(CH_2)_4$ (**h**), $(CH_2)_{11}$ (**i**).

was extended to a number of ketones. The three-component condensation of tetracyanoethylene with cyclohexanone, substituted cyclohexanones, and cyclododecanone in the presence of ammonium acetate gave malononitriles **IIe**–**IIi** in 49–65% yield. As in the case of aldehydes, compound **IIe**–**IIi** were also obtained from the corresponding ketones and aminoethenetricarbonitrile **I** (yield 52–82%; Scheme 4). These data confirmed that the process may involve intermediate formation of imines **A**, for cyclic ketones cannot be transformed into Schiff bases like **III**.

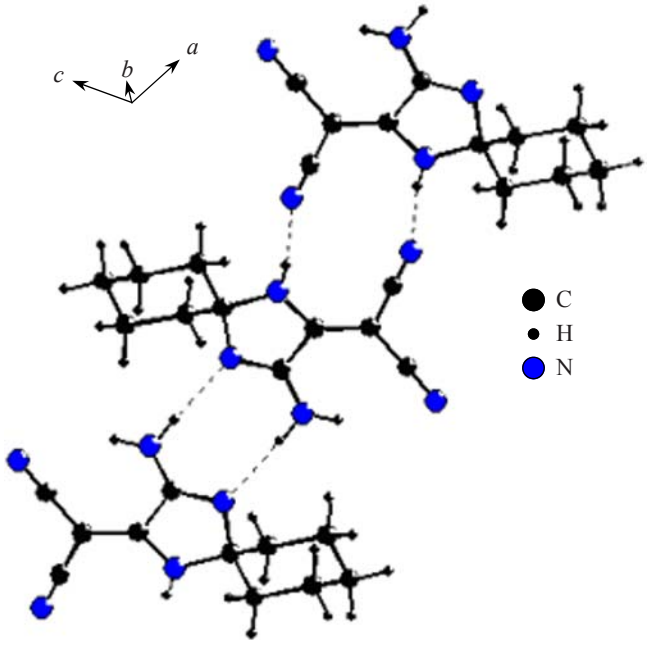



**Fig. 3.** Intermolecular hydrogen bonds in the crystalline structure of 2-(3-amino-1,4-diazaspiro[4.5]dec-3-en-2-ylidene)-malononitrile (**IIe**).

Thus we succeeded in effecting self-assembly of 2,5-dihydro-1*H*-imidazole ring along three approaches: (1) direct synthesis from tetracyanoethylene, aldehyde, and ammoniun acetate (Schemes 1, 4); (2) two-step process with preliminary isolation of intermediate aminoethenetricarbonitrile **I** (Schemes 2, 4); and (3) reaction of preliminarily prepared aminoethenetricarbonitrile **I** with 1,3,5-trisubstituted 2,4-diazapenta-1,4-dienes (Scheme 3).

The structure of compound **IIe** was determined by X-ray analysis (Fig. 2). The geometric parameters of molecule **IIe** (bond lengths and bond angles) did not fall out of the corresponding standard ranges [13]. The crystalline structure of compound **IIe** is characterized by formation of centrosymmetric dimers via strong intermolecular hydrogen bonds (Fig. 3).

The structure of compounds **IIa**–**IIi** was also confirmed by the IR, $^1H$ NMR, and mass spectra. Their IR spectra contained strong absorption bands in the region 3100–3500 $cm^{-1}$ due to stretching vibrations of the N–H bonds and bands at 1645–1650 $cm^{-1}$ due to vibra-

tions of the C=N bonds. Conjugated cyano groups gave rise to medium-intensity bands in the region 2210–2230 $cm^{-1}$, and stretching vibrations of the double C=C bond appeared at 1590–1600 $cm^{-1}$.

Compounds **IIa**–**IIi** displayed in the $^1H$ NMR spectra a singlet at δ 12.10–11.40 ppm from the NH proton in the imidazole ring and a singlet at δ 6.4–6.25 ppm from the amino group. In the spectrum of **IIi**, the amino group protons resonated at δ 5.02 ppm. Signals from the 2-H proton in the imidazole ring of compounds **IIa**–**IIc** appeared in the $^1H$ NMR spectra as a doublet of doublets at δ 5.4–5.2 ppm, and the corresponding signal of 2-phenyl derivative **IIc** was a doublet at δ 6.22 ppm. In the mass spectra of **IIa**–**IIi**, the molecular ion peak had a relative intensity of 15–95%.

From the viewpoint of modern synthetic chemistry, imidazole ring is built up via heterocyclization processes [14]. The main reagent for the synthesis of imidazoles containing cyano groups is diaminoethylenedicarbonitrile [15–17]. This reagent ensures imidazole ring closure through simultaneous formation of *1–2* and *2–3* bonds. Therefore, the described synthetic approach to partially hydrogenated aminoimidazoles on the basis of previously unknown aminotricyanoethylene **I** seems to be unusual, for it involves formation of *1–2* and *3–4* (or *1–5* and *2–3*) bonds. It is also interesting that intramolecular heterocyclization of intermediate **B** results in the formation of five-membered imidazole heteroring, whereas enamino nitrile fragment typically gives rise to six-membered (pyrimidine) ring [18–21]. In the examined reactions, the cyclization involves the $C^3{\equiv}N^1$ group attached to the same carbon atom as the amino group rather than that in the dicyanomethylidene fragment. The observed regioselectivity may be rationalized by increased electron density on the $C^4$ and $C^5$ atoms due to strong *n*,π-conjugation between the amino group and two cyano groups on $C^1$. On the other hand, the $C^3{\equiv}N^1$ group (Fig. 1) is not involved in such conjugation, so that it is activated toward nucleophilic attack.

The X-ray diffraction data (Table 1) support the above stated. The formally single $C^2$–$N^4$ bond in molecule **I** is shortened to 1.326(2) Å, while the formally double $C^1{=}C^2$ bond is extended to 1.366(2) Å; in addition, the C–CN bonds are nonequivalent ($C^2$–$C^3$ 1.462, $C^1$–$C^4$ 1.421, $C^1$–$C^5$ 1.430 Å). We believe that the reason is strong *n*,π-conjugation in the molecule. One more evidence is provided by the planar structure of the amino group (the sum of the bond angles at the $N^4$ atom is 360°). The formation of intermolecular hydrogen bond system (Fig. 4) also counts in favor of conjugation leading to increase in the electron density on the $C^4{\equiv}N^2$ and $C^5{\equiv}N^3$ cyano groups [22].

**Table 1.** Bond lengths (*d*) and bond angles (ω) in the molecule of 2-aminoethene-1,1,2-tricarbonitrile (**I**)

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| $N^4$–$C^2$ | 1.326(2) | $C^2{=}C^1$ | 1.366(2) |
| $N^1{\equiv}C^3$ | 1.131(3) | $C^2$–$C^3$ | 1.462(2) |
| $N^2{\equiv}C^4$ | 1.136(2) | $C^1$–$C^4$ | 1.421(2) |
| $N^3{\equiv}C^5$ | 1.138(2) | $C^1$–$C^5$ | 1.430(2) |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| $C^2N^4H^1$ | 118.5(14) | $C^2C^1C^4$ | 120.34(15) |
| $C^2N^4H^2$ | 120.0(19) | $C^2C^1C^5$ | 122.94(14) |
| $H^1N^4H^2$ | 121(2) | $C^4C^1C^5$ | 116.72(15) |
| $N^4C^2C^1$ | 127.07(15) | $N^1C^3C^2$ | 178.7(2) |
| $N^4C^2C^3$ | 116.27(15) | $N^2C^4C^1$ | 177.2(2) |
| $C^1C^2C^3$ | 116.65(14) | $N^3C^5C^1$ | 176.56(19) |

We also calculated the charges on atoms in molecule **I** at the B3LYP/6-311G level using Gaussian 98 software (Table 2). Analogous calculations were performed for ethene-1,1,2-tricarbonitrile (**IV**) with a view to elucidate how the presence of amino group affects charge distribution in the molecule of 2-aminoethene-1,1,2-tricarbonitrile (**I**). The results showed that the negative charges on the $N^2$ and $N^3$ atoms (for atom numbering, see Fig. 1) in molecule **I** are larger than those found for molecule **IV**, while the negative charge on $N^1$ in molecule **I** is lower than that in molecule **IV**. Thus participation of just the $N^2$ and $N^3$ atoms in intra-

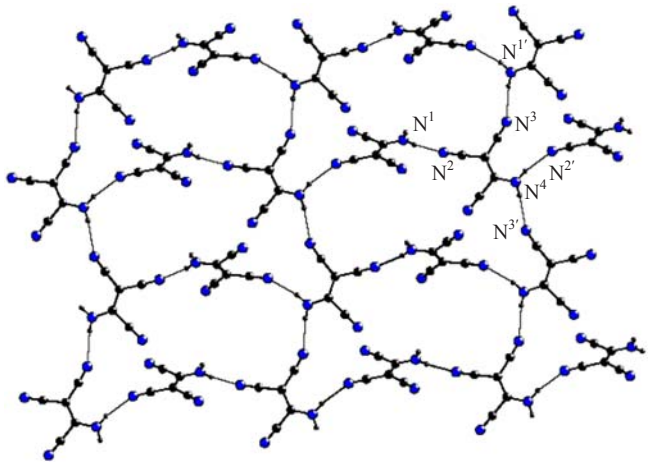



**Fig. 4.** Intermolecular hydrogen bonds in the crystalline structure of 2-aminoethene-1,1,2-tricarbonitrile (**I**).

**Table 2.** Charges on atoms in the molecules of 2-aminoethene-1,1,2-tricarbonitrile (**I**) and ethene-1,1,2-tricarbonitrile (**IV**)

| Atom | I | IV | Atom | I | IV |
|---|---|---|---|---|---|
| $C^1$ | +0.004 | +0.069 | $C^5$ | +0.071 | +0.093 |
| $C^2$ | +0.354 | +0.054 | $N^1$ | −0.162 | −0.177 |
| $C^3$ | +0.048 | +0.056 | $N^2$ | −0.196 | −0.167 |
| $C^4$ | +0.026 | +0.067 | $N^3$ | −0.201 | −0.177 |

molecular hydrogen bonding (X-ray diffraction data, Fig. 4) is consistent with the calculated electron density distribution [22].

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The $^1$H NMR spectra were measured on a Bruker AM-500 spectrometer (500.13 MHz) using DMSO-$d_6$ as solvent. The molecular weights were determined from the mass spectra (electron impact, 70 eV) which were obtained on a Finnigan Mat Incos 50 instrument. X-Ray diffraction data for single crystals of compounds **I** and **IIe** were acquired on an Enraf–Nonius CAD-4 four-circle diffractometer (Mo$K_\alpha$ irradiation, graphite monochromator, ω-scanning). The unit cell parameters were determined and refined using 25 reflections in the Θ range from 11 to 20°. The structures were solved, and the positional and thermal parameters of atoms were refined, using SHELXL97 software package [23]. Hydrogen atoms were localized by Fourier difference syntheses, and their positions were refined in isotropic approximation. The positions and thermal vibration tensors of non-hydrogen atoms were refined in full-matrix anisotropic approximation. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates.

**2-Aminoethene-1,1,2-tricarbonitrile (I).** Tetracyanoethylene, 0.64 g (0.005 mol), was added under stirring to a suspension of 0.97 g of ammonium acetate in 5 ml of 1,4-dioxane. After 20 min (test with hydroquinone, TLC), the mixture was filtered, 0.5 g of methyl iodide was added to the filtrate, and the solvent was removed under reduced pressure. The residue was ground with hexane, and the precipitate was filtered off. Yield 0.55 g (94%). Yellow crystals of **I** suitable for X-ray analysis were grown from a solution in dioxane. Rhombic crystals, space group $Pca2_1$; unit cell parameters: $a$ = 13.3146(8), $b$ = 5.7488(4), $c$ = 7.1774(6) Å; $Z$ = 4; divergence factor $R$ = 0.032.

**2-(4-Amino-2-isopropyl-2,5-dihydro-1*H*-imidazol-5-ylidene)malononitrile (IIa).** *a*. Tetracyanoethylene, 0.64 g (5 mmol), was dissolved in 5 ml of dioxane, 1 g of ammonium acetate and 0.36 g (5 mmol) of isobutyraldehyde were added, and the mixture was stirred for 6 h until negative test for tetracyanoethylene (with hydroquinone). The mixture was diluted with water, and the precipitate was filtered off, washed with water and propan-2-ol, and recrystallized from propan-2-ol. Yield 42%.

*b*. Compound **I**, 0.29 g (2.5 mmol), was added under stirring to a suspension of 0.5 g of ammonium acetate and 0.18 g (2.5 mmol) of isobutyraldehyde in 5 ml of dioxane. When the reaction was complete (TLC), the mixture was diluted with water, and the precipitate was filtered off, washed with water and propan-2-ol, and recrystallized from propan-2-ol. Yield 56%.

*c*. Compound **I**, 0.29 g (2.5 mmol), and Schiff base **IIIa**, 0.33 g (1.7 mmol), were dissolved in 5 ml of dioxane. After 3 h, the mixture was diluted with water, and the precipitate was filtered off, washed with water and propan-2-ol, and recrystallized from propan-2-ol. Yield 63%, mp 202–203°C. IR spectrum, ν, cm$^{-1}$: 3460, 3280–3100 (NH, $NH_2$); 2225, 2220 (C≡N); 1645 (C=N). $^1$H NMR spectrum, δ, ppm: 11.40 d (1H, NH), 6.43 s (2H, $NH_2$), 5.21 d.d (1H, 2-H), 2.04 m [1H, C**H**$(CH_3)_2$], 0.95 d (3H, $CH_3$, $J$ = 6.7 Hz), 0.72 d (3H, $CH_3$, $J$ = 6.7 Hz). Mass spectrum: $m/z$ 189 ($I_{rel}$ 15%) $[M]^+$. Found, %: C 57.02; H 5.75; N 37.03. $C_9H_{11}N_5$. Calculated, %: C 57.13; H 5.86; N 37.01. $M$ 189.22.

Compounds **IIb**–**IIi** were synthesized in a similar way.

**2-[4-Amino-2-(1-ethylpropyl)-2,5-dihydro-1*H*-imidazol-5-ylidene]malononitrile (IIb).** Yield 40 (*a*), 49 (*b*), 55% (*c*); mp 209–210°C. IR spectrum, ν, cm$^{-1}$: 3430, 3280–3100 (NH, $NH_2$); 2225, 2220 (C≡N); 1650 (C=N). $^1$H NMR spectrum, δ, ppm: 11.42 d (1H, NH), 6.38 s (2H, $NH_2$), 5.41 d.d (1H, 2-H), 1.62 m [1H, C**H**$(CH_2)_2$], 1.35 m (2H, CHC**H**$_2$CH$_3$), 1.10 m (2H, CHC**H**$_2$CH$_3$), 0.95 t (3H, $CH_3$, $J$ = 7.3 Hz), 0.85 t (3H, $CH_3$, $J$ = 7.3 Hz). Mass spectrum: $m/z$ 217 ($I_{rel}$, 14%) $[M]^+$. Found, %: C 60.71; H 6.85; N 32.03. $C_{11}H_{15}N_5$. Calculated, %: C 60.81; H 6.96; N 32.23. $M$ 217.27.

**2-[5-Amino-2-(1-ethylpentyl)-2,5-dihydro-1*H*-imidazol-5-ylidene]malononitrile (IIc).** Yield 36 (*a*), 42 (*b*), 57% (*c*); mp 209–210°C. IR spectrum, ν, cm$^{-1}$: 3430, 3280–3100 (NH, $NH_2$); 2225, 2220 (C≡N); 1650 (C=N). $^1$H NMR spectrum, δ, ppm: 11.39 d (1H, NH), 6.39 s (2H, $NH_2$), 5.40 d.d (1H, 2-H), 1.66 m [1H,

C**H**$(CH_2)_2$], 1.4–0.8 m (14H, $CH_2$, $CH_3$). Mass spectrum: *m*/*z* 245 ($I_{rel}$ 10%) $[M]^+$. Found, %: C 63.59; H 7.86; N 28.50. $C_{13}H_{19}N_5$. Calculated, %: C 63.65; H 7.81; N 28.55. *M* 245.32.

**2-(5-Amino-2-phenyl-2,5-dihydro-1*H*-imidazol-5-ylidene)malononitrile (IId).** Yield 40 (*a*), 59% (*b*); mp 208–209°C. IR spectrum, ν, $cm^{-1}$: 3450, 3330–3100 (NH, $NH_2$); 2230, 2210 (C≡N); 1650 (C=N). $^1$H NMR spectrum, δ, ppm: 12.10 d (1H, NH), 7.81 d (2H, *o*-H, *J* = 7.4 Hz), 7.41 t (2H, *m*-H, *J* = 7.4 Hz), 7.28 t (1H, *p*-H, *J* = 7.4 Hz), 6.22 d (1H, 2-H), 5.05 s (2H, $NH_2$). Mass spectrum: *m*/*z* 223 ($I_{rel}$ 50%) $[M]^+$. Found, %: C 64.52; H 4.13; N 31.31. $C_{12}H_9N_5$. Calculated, %: C 64.56; H 4.06; N 31.37. *M* 223.24.

**2-(3-Amino-1,4-diazaspiro[4.5]dec-3-en-2-ylidene)malononitrile (IIe).** Yield 62 (*a*), 72% (*b*); mp 198–199°C. IR spectrum, ν, $cm^{-1}$: 3440, 3280–3100 (NH, $NH_2$); 2225, 2210 (C≡N); 1645 (C=N). $^1$H NMR spectrum, δ, ppm: 11.41 s (1H, NH), 6.25 s (2H, $NH_2$), 1.8–1.2 m (10H, $CH_2$). Mass spectrum: *m*/*z* 215 ($I_{rel}$ 52%) $[M]^+$. Found, %: C 61.23; H 5.93; N 32.47. $C_{11}H_{13}N_5$. Calculated, %: C 61.38; H 6.09; N 32.54. *M* 215.26. Crystallographic data: *a* = 20.7450(7), *b* = 5.822(1), *c* = 20.852(1) Å; β = 116.10(1)°; *Z* = 8; space group *C*12/*c*1; divergence factor *R* = 0.051.

**2-(3-Amino-8-methyl-1,4-diazaspiro[4.5]dec-3-en-2-ylidene)malononitrile (IIf).** Yield 65 (*a*), 80% (*b*); mp 196–197°C. IR spectrum, ν, $cm^{-1}$: 3460, 3280–3100 (NH, $NH_2$); 2235, 2200 (C≡N); 1665 (C=N). $^1$H NMR spectrum, δ, ppm: 11.45 s (1H, NH), 6.34 s (2H, $NH_2$), 1.9–1.2 m (9H, CH, $CH_2$), 0.90 d (3H, $CH_3$, *J* = 6.8 Hz). Mass spectrum: *m*/*z* 229 ($I_{rel}$ 45%) $[M]^+$. Found, %: C 62.86; H 6.69; N 30.43. $C_{12}H_{15}N_5$. Calculated, %: C 62.86; H 6.59; N 30.54. *M* 229.28.

**2-(3-Amino-8-phenyl-1,4-diazaspiro[4.5]dec-3-en-2-ylidene)malononitrile (IIg).** Yield 54 (*a*), 66% (*b*); mp 208–209°C. IR spectrum, ν, $cm^{-1}$: 3500, 3400, 3280–3100 (NH, $NH_2$); 2225, 2200 (C≡N); 1650 (C=N). $^1$H NMR spectrum, δ, ppm: 11.53 s (1H, NH), 11.53 s (1H, NH), 7.30 t (2H, *m*-H, *J* = 7.4 Hz), 7.24 d (2H, *o*-H, *J* = 7.4 Hz), 7.19 t (1H, *p*-H, *J* = 7.4 Hz), 6.43 s (2H, $NH_2$), 2.63 m (1H, 2-H), 2.1–1.35 m (8H, $CH_2$). Mass spectrum: *m*/*z* 291 ($I_{rel}$ 95%) $[M]^+$. Found, %: C 69.95; H 5.93; N 23.90. $C_{17}H_{17}N_5$. Calculated, %: C 70.08; H 5.88; N 24.04. *M* 291.36.

**2-(3-Amino-6-methyl-1,4-diazaspiro[4.5]dec-3-en-2-ylidene)malononitrile (IIh).** Yield 62 (*a*), 82% (*b*); mp 194–195°C. IR spectrum, ν, $cm^{-1}$: 3420, 3280–3100 (NH, $NH_2$); 2225, 2210 (C≡N); 1645 (C=N). $^1$H NMR spectrum, δ, ppm: 11.35 s (1H, NH), 6.44 s (2H, $NH_2$), 1.9–1.2 m (9H, CH, $CH_2$), 0.4 d (3H, $CH_3$). Mass spectrum: *m*/*z* 229 ($I_{rel}$ 47%) $[M]^+$. Found, %: C 62.83; H 6.64; N 30.49. $C_{12}H_{15}N_5$. Calculated, %: C 62.86; H 6.59; N 30.54. *M* 229.28.

**2-(3-Amino-1,4-diazaspiro[4.11]hexadec-3-en-2-ylidene)malononitrile (IIi)**. Yield 49 (*a*), 52% (*b*); mp 205–206°C. IR spectrum, ν, $cm^{-1}$: 3500, 3400, 3280–3100 (NH, $NH_2$); 2225, 2210 (C≡N); 1645 (C=N). $^1$H NMR spectrum, δ, ppm: 11.51 s (1H, NH), 6.25 s (2H, $NH_2$), 1.7–1.25 m (22H, $CH_2$). Mass spectrum, *m*/*z* 299 ($I_{rel}$ 24%) $[M]^+$. Found, %: C 68.02; H 8.50; N 23.30. $C_{17}H_{25}N_5$. Calculated, %: C 68.19; H 8.42; N 23.39. *M* 299.41.

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