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Synthesis of 2,2,3,3-Tetracyanocyclopropyl Ketones and Their Reactions with Oxygen-Centered Nucleophiles

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Abstract—A procedure for the synthesis of 2,2,3,3-tetracyanocyclopropyl ketones has been developed on the basis of three-component Wideqvist reaction of dihydroxymethyl ketones, 2-bromomalononitrile, and malononitrile. The presence of five electron-withdrawing groups in the resulting cyclopropyl ketones determines high acidity of proton in the cyclopropane ring. Facile deprotonation by the action of bases promotes opening of the three-membered ring with formation of either 1,1,3,3-tetracyanopropenides or (in the presence of alcohols or oximes), [2-alkoxy(aminooxy)-5-amino-4-cyanofuran-3(2*H*)-ylidene]malononitriles. The reaction with acetone oxime was not accompanied by cleavage of the three-membered ring, and nucleophilic attack was directed at the cyano groups in the *trans* position with respect to the carbonyl group to give the corresponding (1*R**,5*S**,6*R**)-4-amino-2,2-bis(prop-2-ylideneaminooxy)-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitriles.

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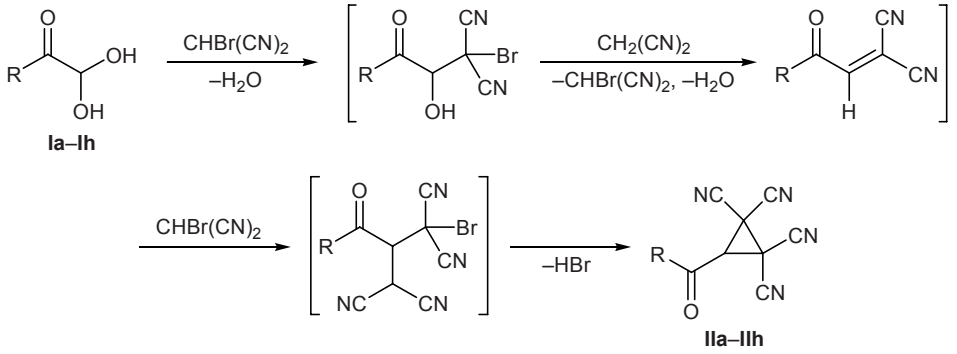
One of the main procedures for the synthesis of 1,1,2,2-tetracyanocyclopropanes is based on the Wideqvist reaction which implies treatment of carbonyl compounds with 2-bromomalononitrile in aqueous alcohol at room temperature over a period of 0.5–12 h in the presence of potassium iodide as reducing agent [1–4]. However, the scope of this procedure is essentially limited: it cannot be used for the synthesis of tetracyanocyclopropanes having five or six electron-withdrawing substituents. Potassium iodide is capable of reacting with cyclopropanes, leading to cleavage of the three-membered ring with formation of cyano-substituted propenides [5–8].

As we showed previously, activated carbonyl compounds that could give rise to stable hydrates may be converted into tetracyanocyclopropanes via reaction with 2-bromomalononitrile in the absence of potassium iodide [9, 10]. It was presumed that in this case bromomalononitrile acts as reducing agent thus being oxidized to dibromomalononitrile. Using this procedure we successfully synthesized a series of 3-aroylcyclopropane-1,1,2,2-tetracarbonitriles [10]. We pro-

Scheme 1.



Ia–Ih **IIa–IIh**

R = Ph (**a**), 4-BrC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 3,4-$(MeO)_2C_6H_3$ (**d**), 3-$O_2NC_6H_4$ (**e**), Me (**f**), *t*-Bu (**g**), 2-thienyl (**h**).

posed to use malononitrile as reducing agent; during the reaction it is converted into bromomalononitrile which may return to the process. Our new approach to the synthesis of cyclopropanes is based on three-component reaction of dihydroxymethyl ketone **Ia**–**Ih** with malononitrile and 2-bromomalononitrile at a ratio of 1:1:1. The yields of 2,2,3,3-tetracyanocyclopropyl ketones **IIa**–**IIh** obtained in such a way were 68–82%. Phenylglyoxal failed to react with malononitrile (in contrast to bromomalononitrile) in the absence of a catalyst; therefore, we presumed that the reaction begins just with attack on bromomalononitrile and that malononitrile acts as reducing and debrominating agent (Scheme 1).

The structure of cyclopropanes **IIa**–**IIh** was confirmed by the IR, ^{1}H NMR, and mass spectra. All compounds **IIa**–**IIh** possess a hydrogen atom in the three-membered ring; it gives rise to a singlet at δ 5.32–5.66 ppm in the ^{1}H NMR spectra, and the IR spectra contain an absorption band at 3023–3061 cm^{-1} due to stretching vibrations of the C–H bond. In addition, absorption bands belonging to unconjugated cyano groups and carbonyl group were present in the regions 2260–2271 and 1652–1729 cm^{-1}, respectively, and signals from protons in alkyl, aryl, or thiophene substituents were observed in the ^{1}H NMR spectra. All cyclopropanes **II** (except for **IIg**) displayed in the mass spectra molecular ion peaks with low to medium intensity (10–45%).

It is known that electron-deficient cyclopropanes having four and more electron-withdrawing groups exhibit high reactivity toward nucleophiles [5–8, 11–17]. The direction and depth of their transformations in reactions with nucleophiles are largely determined by the nature of nucleophile and electron-withdrawing groups in the substrate. Two main reaction directions are usually considered. The first of these involves initial attack by nucleophile on carbon atoms in the three-membered ring, leading to opening of the latter [5–8], while the second begins with attack on electron-withdrawing group (carbonyl or cyano), and such reactions often occur with conservation of the cyclopropane ring [11–15].

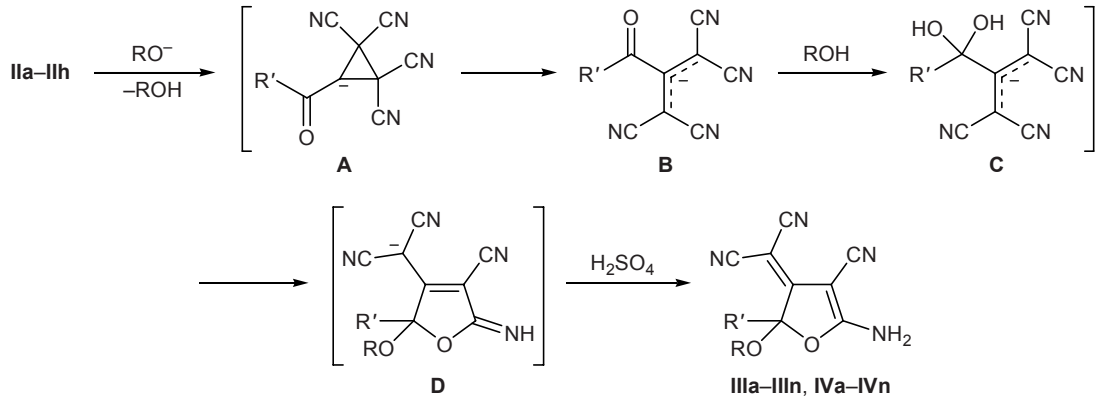
One more reaction direction is possible; it involves carbanion ring cleavage which is likely to follow four-electron electrocyclic mechanism [5, 16–18]. Such reactions are favored by the presence of electron-withdrawing groups which stabilize the resulting allyl-type anion, i.e., propenide. Most frequently, carbanion cleavage preceded formation of cyclopropyl anion in analogous transformations reported until recently. An example is the reaction of tetracyanocyclopropane-1,1-dicarboxylate with ammonia, which resulted in the formation of ammonium 1,1,3,3-tetracyano-2-ethoxycarbonylpropenide [19]. Likewise, pentacyanopropenide and products of its further transformations were formed in reactions of pentacyanocyclopropanecarboxylate with some nucleophiles [17]. In the case of tetracyanocyclopropanes obtained from acetylacetone [16], dimedone [20], and indandione [14], such reactions are preceded by acyl cleavage. Cyclopropyl anion can be generated as intermediate by the action of bases on cyclopropanes having five electron-withdrawing groups. We recently showed that 3-benzoylcyclopropane-1,1,2,2-tetracarbonitrile reacts with alkoxides to give dihydrofuran derivatives, presumably through intermediate formation of cyclopropanide and propenide [21].

Our study on reactions of tetracyanocyclopropyl ketones **IIa**–**IIh** with alkoxides and oximates showed that the formation of dihydrofuran derivatives is general. Cyclopropyl ketones **IIa**–**IIh** reacted with sodium methoxide and sodium 2-hydroxyethoxide in the corresponding alcohols to give (after neutralization with an acid) [2-alkoxy-5-amino-4-cyanofuran-3(2*H*)-ylidene]-malononitriles **IIIa**–**IIIn**, while in the reactions with acetone and acetaldehyde oxime sodium salts [5-amino-4-cyano-2-(alkylideneaminooxy)furan-3(2*H*)-ylidene}malononitriles **IVa**–**IVn** were obtained in 19–87% yields (Scheme 2).

The structure of compounds **IIIa**–**IIIn** and **IVa**–**IVn** was confirmed by the IR, ^{1}H NMR, and mass spectra. In the IR spectra of these compounds, stretching vibrations of conjugated cyano groups gave rise to absorption bands in the region 2203–2225 cm^{-1}; absorption bands at 3074–3280 cm^{-1} were assigned to stretching vibrations of the amino group; and the C=C bond in the dicyanomethylene fragment was characterized by absorption at 1669–1695 cm^{-1}. The ^{1}H NMR spectra contained downfield signals from protons in the amino group (δ 10.12–10.49 ppm) and signals from alkyl, aryl, or thienyl substituent.

Due to effect of five electron-withdrawing substituents, the hydrogen atom in the cyclopropane ring of 2,2,3,3-tetracyanocyclopropyl ketones **IIa**–**IIh** becomes so labile that it can readily be removed as proton by the action of bases. Its acidity also follows from downfield position of its signal in the ^{1}H NMR spectrum (δ 5.32–5.66 ppm). Presumably, in the first step alkoxide (oximate) as a base abstracts proton from cyclopropane **IIa**–**IIh** to afford cyclopropanide **A**

Scheme 2.

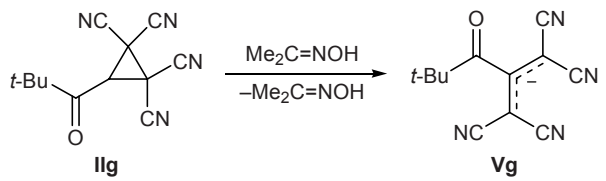


III, R = Me, R′ = Ph (**a**), 4-BrC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 3,4-$(MeO)_2C_6H_3$ (**d**), 3-$O_2NC_6H_4$ (**e**), Me (**f**), *t*-Bu (**g**), 2-thienyl (**h**); R = $HOCH_2CH_2$, R′ = Ph (**i**), 4-BrC_6H_4 (**j**), 4-$MeOC_6H_4$ (**k**), 3,4-$(MeO)_2C_6H_3$ (**l**), Me (**m**), *t*-Bu (**n**); **IV**, R = MeCH=N, R′ = Ph (**a**), 4-BrC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 3,4-$(MeO)_2C_6H_3$ (**d**), Me (**e**), *t*-Bu (**f**), 2-thienyl (**g**); R = Me_2C=N, R′ = Ph (**h**), 4-BrC_6H_4 (**i**), 4-$MeOC_6H_4$ (**j**), 3,4-$(MeO)_2C_6H_3$ (**k**), 3-$O_2NC_6H_4$ (**l**), Me (**m**), 2-thienyl (**n**).

which undergoes opening of the three-membered ring (probably following electrocyclic mechanism) with formation of resonance-stabilized propenide ion **B**. Next follows nucleophilic addition of oxygen-centered nucleophile (alcohol or oxime) at the carbonyl group, leading to hemiacetal **C**, and subsequent heterocyclization involving the hydroxy group and spatially close cyano group gives dihydrofuran derivative **D**. Upon acidification of the reaction mixture anion **D** is converted into final product **IIIa**–**IIIn** or **IVa**–**IVn**.

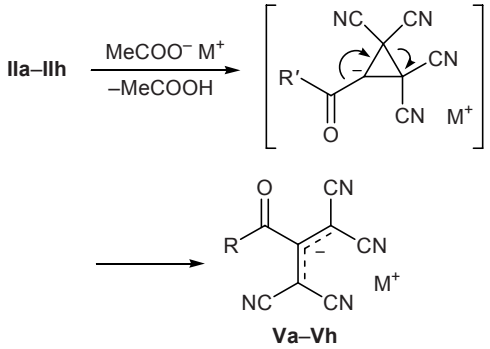
The rate of the reaction of cyclopropanes **IIa**–**IIh** with alkoxides and oximates and the yields of the resulting dihydrofurans depend on both O-nucleophile nature and substituent in the substrate. Nucleophile addition at the carbonyl group is likely to be the slowest process. Therefore, the reaction with the least sterically hindered methyl tetracyanocyclopropyl ketone (**IIf**) is the most facile, and the yield of the corresponding product is the highest. The aromatic ring in cyclopropanes **IIa**–**IIe** does not hamper attack by nucleophile, but donor substituents in the aromatic ring deactivate the carbonyl group, and the reaction rate decreases. The *tert*-butyl radical in cyclopropane **IIg** shields the carbonyl group, so that addition of a bulky nucleophile is hindered, and the reaction (e.g., with acetone oxime sodium salt) stops at the stage of formation of propenide **Vg** (yield 87%), whereas dihydrofuran derivative could not be obtained (Scheme 3).

Scheme 3.



We tried to isolate the corresponding propenides by reacting cyclopropanes **IIa**–**IIh** with compounds that are fairly strong bases but weak nucleophiles. We found that propenides **V** are formed in reactions of cyclopropanes **IIa**–**IIh** sodium or ammonium formates, acetates, and carbonates. The best results were obtained with the use of acetates; 2-acyl-1,1,3,3-tetracyanopropenides **Va**–**Vh** were formed in almost quantitative yield (86–93%; Scheme 4).

Scheme 4.



M = Na (**a**–**e**, **g**, **h**), NH_4 (**f**); R = Ph (**a**, **f**), 4-BrC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 3,4-$(MeO)_2C_6H_3$ (**d**), 3-$O_2NC_6H_4$ (**e**), *t*-Bu (**g**), 2-thienyl (**h**).

The structure of compound **Vf** was proved by X-ray analysis, and the IR spectra of propenides **Va**–**Ve**, **Vg**, and **Vh** were similar to the spectrum of **Vf**. Figure 1 shows the structure of molecule **Vf** with atom numbering. The C^2=O^1 carbonyl group is turned through

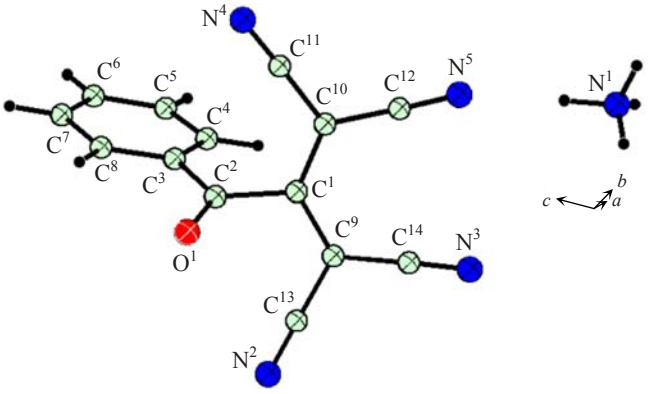
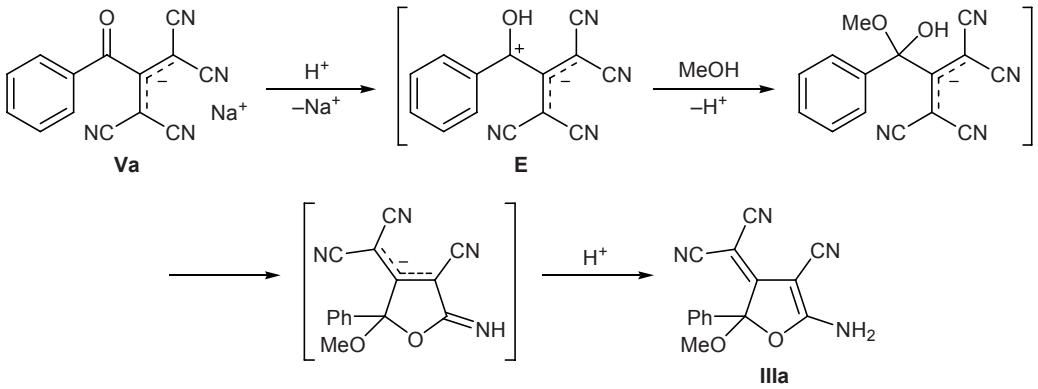


Fig. 1. Structure of the molecule of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide (**Vf**) according to the X-ray diffraction data.

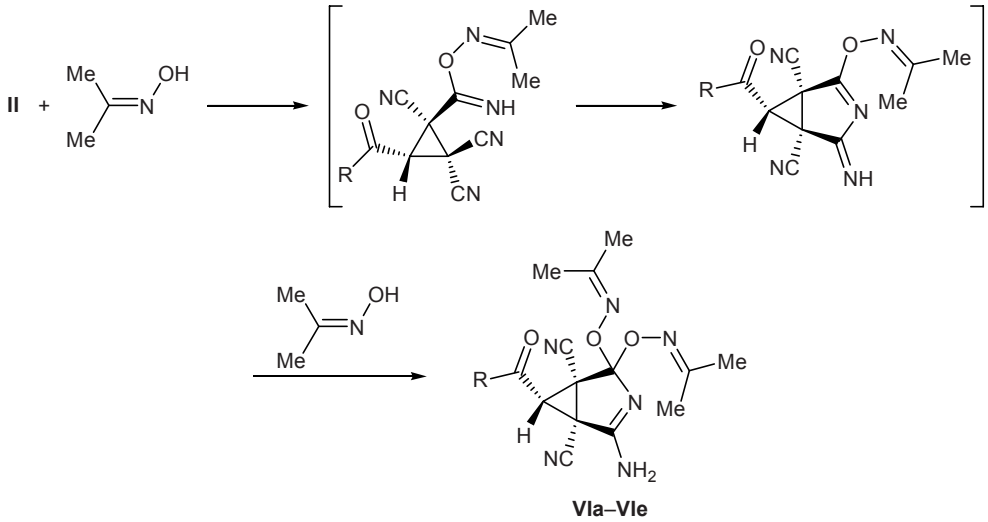
a dihedral angle of 16.3° relative to the benzene ring plane, and the dihedral angle between that group and the tetracyanopropenide fragment is 63.6°. Conjugation of the carbonyl group with the benzene ring is reflected in shortened C^2–O^3 bond [1.473(2) Å] relative to the C^2–C^1 bond [1.522(3) Å]. The dicyanomethyl fragments $C^9(CN)_2$ and $C^{10}(CN)_2$ are turned by an angle of 10.8° with respect to each other due to steric interactions between the $C^{14}{\equiv}N^3$ and $C^{12}{\equiv}N^5$ groups. In crystal, the carbonyl oxygen atom and N^2 and N^5 cyano nitrogen atoms are involved in hydrogen bonding with the ammonium ion (Fig. 2). The O^{1i}, N^{2ii}, and N^{5iii} atoms are characterized by the following symmetry elements: *i*: $1-x, 2-y, -z$; *ii*: $1+x, 1+y, z$; *iii*: $1-x, 3-y, -z$.

The transformation sequence shown in Scheme 2 is confirmed by the reaction of propenide **Va** with methanol in the presence of sodium hydroxide. It was also found that propenide **Va** does not react with methanol in neutral medium but reacts in the presence of sulfuric acid to give 78% of dihydrofuran derivative

Scheme 5.



Scheme 6.



R = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 3,4-$(MeO)_2C_6H_3$ (**c**), *t*-Bu (**d**), 2-thienyl (**e**).

IIIa (Scheme 5). Presumably, acid catalysis implies protonation of propenide **Va** at the carbonyl oxygen atom (rather than at carbon atoms of the allylic fragment) with formation of zwitterionic intermediate **E**.

According to published data, compounds possessing a tetracyanoethyl fragment react with oximes to form pyrrole derivatives [22]. Nucleophilic attack on the carbonyl group in cyclopropyl ketones **II** could give rise to furan derivatives [22]. We found that tetracyanocyclopropanes **IIa**, **IIc**, **IId**, **IIg**, and **IIh** react with acetone oxime in MeCN to give (1*R**,5*S**,6*R**)-4-amino-2,2-bis(prop-2-ylideneaminooxy)-6-R-carbonyl-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitriles **VIa**–**VIe** in 35–73% yield (Scheme 6).

The structure of compounds **VIa**–**VIe** was confirmed by the IR and ^{1}H NMR spectra; in addition, the ^{13}C NMR spectrum of **VIb** was recorded. The IR spectra of these compounds contained an absorption band at 3045–3077 cm^{-1} due to stretching vibrations of the cyclopropane C–H bond, and bands belonging to vibrations of unconjugated cyano groups (2246–2249 cm^{-1}), carbonyl group (1668–1674 cm^{-1}), and amino group (3262–3378 cm^{-1}) were present. The cyclopropane proton signal appeared in the ^{1}H NMR spectra at δ 3.38–4.01 ppm, and protons in the amino group resonated in the region δ 7.48–7.56 ppm.

Closure of pyrrole ring is possible both at the side of the acyl group and at the side of the hydrogen atom. According to the NMR data, only one among possible stereoisomers is formed. The structure of compound **VId** was proved by X-ray analysis (Fig. 3). The interatomic distances and bond angles in molecule **VId** are typical of such compounds, so that no detailed consideration is necessary. Molecules **VId** in crystal are linked to centrosymmetric dimers via hydrogen bonds N^6–$H^{62}\cdots N^{1i}$ (1 – *x*, 1 – *y*, –*z*; $N^{1i}\cdots H^{62}$ 2.16 Å, $\angle N^1H^{62}N^{1i}$ 165°). Thus the addition occurs at the side opposite to the acyl group, which is likely to be determined by steric factor.

EXPERIMENTAL

The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates; spots were visualized under UV light, by treatment with iodine vapor, or by heating. The IR spectra were recorded from samples dispersed in mineral oil on an FSM-1202 spectrometer with Fourier transform. The ^{1}H NMR spectra were measured on a Bruker DRX-500 spectrometer (500.13 MHz)

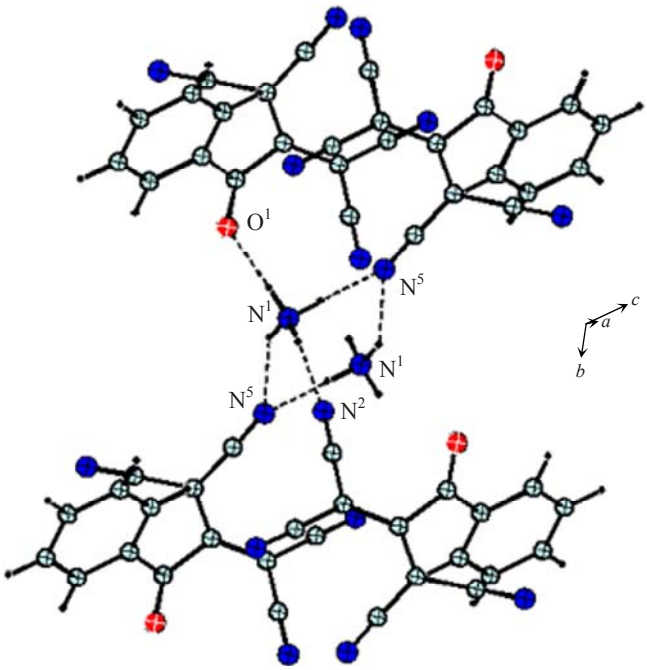


Fig. 2. Hydrogen bonds between the anions and cations in the crystalline structure of ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide (**Vf**).

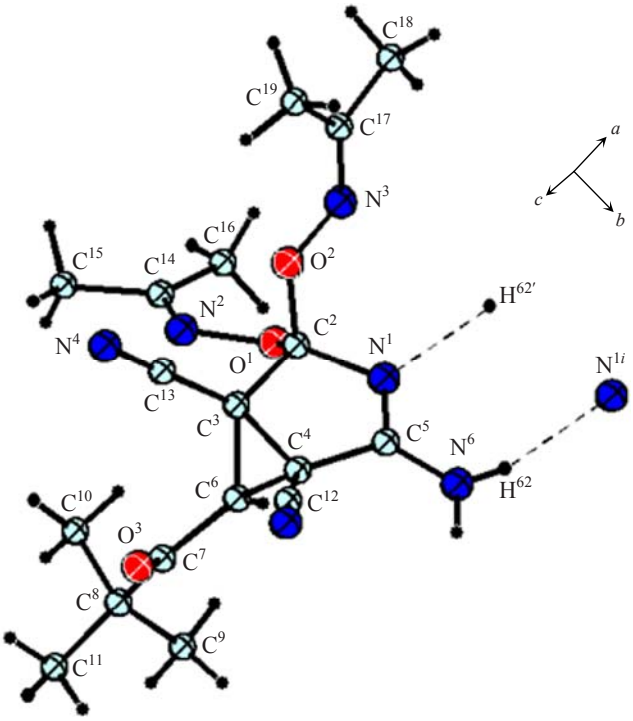


Fig. 3. A fragment of centrosymmetric dimer formed by molecules of 4-amino-2,2-bis(isopropylideneaminooxy)-6-(2,2-dimethyl-1-oxopropyl)-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitrile (**VId**) in crystal. Molecular structure of one molecule is shown; the $H^{62'}$ and N^{1i} atoms belong to the other molecule.

using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 instrument.

The X-ray diffraction data were acquired from single crystals of compounds **Vf** and **VId** on an Enraf–Nonius CAD-4 four-circle automatic diffractometer (CuK_α irradiation for **Vf** and MoK_α irradiation for **VId**, graphite monochromator, ω-scanning). The structures were solved by the direct methods using SHELXS-97 software package. The positions and thermal parameters of non-hydrogen atoms were refined in full-matrix anisotropic approximation. Hydrogen atoms in structure **Vf** were localized from the Fourier difference syntheses, and their positions were refined in isotropic approximation. The positions of hydrogen atoms in structure **VId** were calculated and refined using the riding model. The crystallographic data for compounds **Vf** and **VId** were deposited to the Cambridge Crystallographic Data Centre, entry nos. CCDC 694326 (**Vf**) and 694327 (**VId**), and are available upon request (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; *http://www.ccdc.cam.ac.uk*; fax: +(44123)333 6033; e-mail: *deposit@ccdc.cam.ac.uk*;).

3-Benzoylcyclopropane-1,1,2,2-tetracarbonitrile (IIa). 2,2-Dihydroxy-1-phenylethanone, 1.52 g (0.01 mol), and malononitrile, 0.66 g (0.01 mol), were dissolved in 15 ml of isopropyl alcohol, 1.45 g (0.01 mol) of 2-bromomalononitrile was added to the solution under stirring, and the mixture was stirred for 15 min. The precipitate was filtered off and washed with isopropyl alcohol. Yield 1.92 g (78%), mp 211–212°C (decomp.) [10].

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

3-(4-Bromobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIb). Yield 82%, mp 214–215°C (decomp.) [10].

3-(4-Methoxybenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIc). Yield 76%, mp 204–205°C (decomp.) [10].

3-(3,4-Dimethoxybenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IId). Yield 75%, mp 186–187°C (decomp.). IR spectrum, ν, cm^{-1}: 3027 (C–H), 2261 (C≡N), 1673 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.86 s and 3.9 s (3H each, OCH_3); 5.66 s (1H, CH); 7.19 d, 7.65 s, and 7.98 d (3H, C_6H_3). Mass spectrum: *m*/*z* 306 (I_{rel} = 10%). Found, %: C 62.75; H 3.32; N 18.33. $C_{16}H_{10}N_4O_3$. Calculated, %: C 62.74; H 3.29; N 18.29.

3-(3-Nitrobenzoyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIe). Yield 78%, mp 219–220°C (decomp.). IR spectrum, ν, cm^{-1}: 3061 (C–H), 2271 (C≡N), 1698 (C=O). ^{1}H NMR spectrum, δ, ppm: 5.88 s (1H, CH); 7.96 t, 8.42 d, 8.57 s, and 8.61 d (4H, C_6H_4). Mass spectrum: *m*/*z* 291 (I_{rel} = 15%). Found, %: C 57.80; H 1.68; N 24.01. $C_{14}H_5N_5O_3$. Calculated, %: C 57.74; H 1.73; N 24.05.

3-Acetylcyclopropane-1,1,2,2-tetracarbonitrile (IIf). Yield 68%, mp 182–183°C (decomp.); published data [23]: mp 196–197°C (decomp.).

3-(2,2-Dimethyl-1-oxopropyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIg). Yield 73%, mp 204–205°C (decomp.); published data [23]: mp 166–167°C (decomp.).

3-(2-Thienylcarbonyl)cyclopropane-1,1,2,2-tetracarbonitrile (IIh). Yield 76%, mp 201–202°C (decomp.). IR spectrum, ν, cm^{-1}: 3061 (C–H), 2260 (C≡N), 1652 (C=O). ^{1}H NMR spectrum, δ, ppm: 5.54 s (1H, CH); 7.40 t, 8.27 d, 8.55 d (3H, C_4H_3S). Mass spectrum: *m*/*z* 252 (I_{rel} = 45%). Found, %: C 57.10; H 1.66; N 22.23. $C_{12}H_4N_4OS$. Calculated, %: C 57.14; H 1.60; N 22.21.

2-[5-Amino-4-cyano-2-methoxy-2-phenylfuran-3(2*H*)-ylidene]malononitrile (IIIa). *a*. A suspension of 2.46 g (0.01 mol) of cyclopropane **Ia** in 10 ml of methanol was added under stirring to a solution of 0.05 g (0.02 mol) of sodium in 10 ml of methanol. The mixture was kept for 24 h, neutralized with 5% sulfuric acid, and extracted with ethyl acetate. The organic phase was dried over calcined sodium sulfate, the solvent was distilled off, and the residue was ground with 10 ml of water. The precipitate was filtered off and washed with water. Yield 2.36 g (83%), mp 138–139°C (decomp.). IR spectrum, ν, cm^{-1}: 3280, 3140 (NH_2); 2225 (C≡N); 1683 (C=C). ^{1}H NMR spectrum, δ, ppm: 3.48 s (3H, OCH_3), 7.52 m (5H, C_6H_5), 10.33 s (2H, NH_2). Mass spectrum, *m*/*z* 278 (I_{rel} = 30%). Found, %: C 64.55; H 3.66; N 20.10. $C_{15}H_{10}N_4O_2$. Calculated, %: C 64.74; H 3.62; N 20.13.

b. A 5% solution of sulfuric acid, 1 ml, was added under stirring to a solution of 2.68 g (0.01 mol) of propenide **Va** in 10 ml of methanol. The mixture was kept for 24 h, diluted with 10 ml of water, and extracted with ethyl acetate. The organic phase was dried over calcined sodium sulfate, the solvent was distilled off, and the residue was ground with 10 ml of water. The precipitate was filtered off and washed with water. Yield 2.87 g (78%), mp 137–138°C (decomp.).

Compounds **IIIb**–**IIIh** were synthesized in a similar way according to method *a*.

2-[5-Amino-2-(4-bromophenyl)-4-cyano-2-methoxyfuran-3(2*H*)-ylidene]malononitrile (IIIb). Yield 79%, mp 205–206°C (decomp.). IR spectrum, ν, cm^{-1}: 3255, 3177 (NH_2); 2219 (C≡N); 1695 (C=C). ^1H NMR spectrum, δ, ppm: 3.48 s (3H, OCH_3), 7.47 d and 7.68 d (2H each, C_6H_4), 10.43 s (2H, NH_2). Found, %: C 50.47; H 2.50; N 15.75. $C_{15}H_9BrN_4O_2$. Calculated, %: C 50.44; H 2.54; N 15.69.

2-[5-Amino-4-cyano-2-methoxy-2-(4-methoxyphenyl)furan-3(2*H*)-ylidene]malononitrile (IIIc). Yield 73%, mp 137–138°C (decomp.). IR spectrum, ν, cm^{-1}: 3261, 3155 (NH_2); 2213 (C≡N); 1677 (C=C). ^1H NMR spectrum, δ, ppm: 3.44 s and 3.79 s (3H each, OCH_3), 7.00 d and 7.44 d (2H each, C_6H_4), 10.29 s (2H, NH_2). Found, %: C 62.37; H 3.94; N 18.20. $C_{16}H_{12}N_4O_3$. Calculated, %: C 62.33; H 3.92; N 18.17.

2-[5-Amino-4-cyano-2-(3,4-dimethoxyphenyl)-2-methoxyfuran-3(2*H*)-ylidene]malononitrile (IIId). Yield 58%, mp 123–124°C (decomp.). IR spectrum, ν, cm^{-1}: 3280, 3198 (NH_2); 2213 (C≡N); 1688 (C=C). ^1H NMR spectrum, δ, ppm: 3.47 s, 3.75 s, and 3.79 s (3H each, OCH_3); 6.94 d, 7.01 d, and 7.07 s (3H, C_6H_3); 10.32 s (2H, NH_2). Found, %: C 60.37; H 4.14; N 16.60. $C_{17}H_{14}N_4O_4$. Calculated, %: C 60.35; H 4.17; N 16.56.

2-[5-Amino-4-cyano-2-methoxy-2-(3-nitrophenyl)furan-3(2*H*)-ylidene]malononitrile (IIIe). Yield 67%, mp 227–228°C (decomp.). IR spectrum, ν, cm^{-1}: 3276, 3178 (NH_2); 2216 (C≡N); 1684 (C=C). ^1H NMR spectrum, δ, ppm: 3.53 s (3H, OCH_3); 7.79 t, 7.95 d, 8.33 s, and 8.38 d (4H, C_6H_4); 10.49 s (2H, NH_2). Mass spectrum: *m*/*z* 323 (I_{rel} = 50%). Found, %: C 55.67; H 2.80; N 21.70. $C_{15}H_9N_5O_4$. Calculated, %: C 55.73; H 2.81; N 21.66.

2-[5-Amino-4-cyano-2-methoxy-2-methylfuran-3(2*H*)-ylidene]malononitrile (IIIe). Yield (87%), mp 239–240°C (decomp.); published data [16]: mp 242–243°C (decomp.).

2-[5-Amino-2-*tert*-butyl-4-cyano-2-methoxyfuran-3(2*H*)-ylidene]malononitrile (IIIg). Yield 74%, mp 200–201°C (decomp.). IR spectrum, ν, cm^{-1}: 3266, 3107 (NH_2); 2217 (C≡N); 1691 (C=C). ^1H NMR spectrum, δ, ppm: 1.00 s (9H, *t*-Bu), 3.37 s (3H, OCH_3), 10.16 s (2H, NH_2). Found, %: C 60.37; H 5.55; N 21.60. $C_{13}H_{14}N_4O_2$. Calculated, %: C 60.45; H 5.46; N 21.69.

2-[5-Amino-4-cyano-2-methoxy-2-(2-thienyl)furan-3(2*H*)-ylidene]malononitrile (IIIh). Yield 76%, mp 147–148°C (decomp.). IR spectrum, ν, cm^{-1}: 3261, 3180 (NH_2); 2218 (C≡N), 1677 (C=C). ^1H NMR spectrum, δ, ppm: 3.45 s (3H, OCH_3); 7.10 t, 7.29 d, and 7.75 d (3H, C_4H_3S); 10.37 s (2H, NH_2). Found, %: C 54.87; H 2.94; N 19.80. $C_{13}H_8N_4O_2S$. Calculated, %: C 54.92; H 2.84; N 19.71.

2-[5-Amino-4-cyano-2-(2-hydroxyethoxy)-2-phenylfuran-3(2*H*)-ylidene]malononitrile (IIIi). A suspension of 2.46 g (0.01 mol) of cyclopropane **Ia** in 10 ml of ethylene glycol was added under stirring to a solution of 0.05 g (0.02 mol) of sodium in 10 ml of ethylene glycol. The mixture was kept for 24 h, neutralized with 5% sulfuric acid, and extracted with ethyl acetate. The organic phase was dried over calcined sodium sulfate, the solvent was distilled off, and the residue was ground with 10 ml of water. The precipitate was filtered off and washed with water. Yield 85%, mp 132–133°C (decomp.). IR spectrum, ν, cm^{-1}: 3270, 3150 (NH_2); 2223 (C≡N); 1685 (C=C). ^1H NMR spectrum, δ, ppm: 3.6–3.72 m (4H, CH_2CH_2), 4.93 t (1H, OH), 7.45–7.57 m (5H, C_6H_5), 10.34 s (2H, NH_2). Mass spectrum: *m*/*z* 308 (I_{rel} = 10%). Found, %: C 62.37; H 3.94; N 18.20. $C_{16}H_{12}N_4O_3$. Calculated, %: C 62.33; H 3.92; N 18.17.

Compounds **IIIj**–**IIIn** were synthesized in a similar way.

2-[5-Amino-2-(4-bromophenyl)-4-cyano-2-(2-hydroxyethoxy)furan-3(2*H*)-ylidene]malononitrile (IIIj). Yield 81%, mp 170–171°C (decomp.). IR spectrum, ν, cm^{-1}: 3255, 3147 (NH_2); 2211 (C≡N); 1690 (C=C). ^1H NMR spectrum, δ, ppm: 3.59–3.68 m (4H, CH_2CH_2), 4.93 t (1H, OH), 7.42 d and 7.70 d (4H, C_6H_4), 10.40 s (2H, NH_2). Found, %: C 49.59; H 2.94; N 14.41. $C_{16}H_{11}BrN_4O_3$. Calculated, %: C 49.63; H 2.86; N 14.47.

2-[5-Amino-4-cyano-2-(2-hydroxyethoxy)-2-(4-methoxyphenyl)furan-3(2*H*)-ylidene]malononitrile (IIIk). Yield 59%, mp 112–113°C (decomp.). IR spectrum, ν, cm^{-1}: 3257, 3160 (NH_2); 2218 (C≡N); 1691 (C=C). ^1H NMR spectrum, δ, ppm: 3.57–3.73 m (4H, CH_2CH_2), 3.80 s (3H, OCH_3), 6.98 d and 7.47 d (2H each, C_6H_4), 10.30 s (2H, NH_2). Found, %: C 60.37; H 4.24; N 16.50. $C_{17}H_{14}N_4O_4$. Calculated, %: C 60.35; H 4.17; N 16.56.

2-[5-Amino-4-cyano-2-(3,4-dimethoxyphenyl)-2-(2-hydroxyethoxy)furan-3(2*H*)-ylidene]malononitrile (IIIl). Yield 42%, mp 115–116°C (decomp.). IR spectrum, ν, cm^{-1}: 3248, 3157 (NH_2); 2212 (C≡N); 1701 (C=C). ^1H NMR spectrum, δ, ppm: 3.59–3.76 m (4H, CH_2CH_2); 3.78 s and 3.80 s (3H each, OCH_3);

6.96 d, 7.02 d, and 7.13 s (3H, C_6H_3); 10.30 s (2H, NH_2). Found, %: C 58.65; H 4.41; N 15.17. $C_{18}H_{16}N_4O_5$. Calculated, %: C 58.69; H 4.38; N 15.21.

2-[5-Amino-4-cyano-2-(2-hydroxyethoxy)-2-methylfuran-3(2*H*)-ylidene]malononitrile (IIIm). Yield 82%, mp 221–222°C (decomp.); published data [16]: mp 212–215°C.

2-[5-Amino-2-*tert*-butyl-4-cyano-2-(2-hydroxyethoxy)furan-3(2*H*)-ylidene]malononitrile (IIIn). Yield 72%, mp 208–209°C (decomp.). IR spectrum, ν, cm^{-1}: 3270, 3100 (NH_2); 2212 (C≡N); 1682 (C=C). ^1H NMR spectrum, δ, ppm: 1.00 s (9H, *t*-Bu), 3.48 t (2H, OC**H**$_2$CH$_2$OH), 3.59 m (2H, OCH$_2$C**H**$_2$OH), 4.76 t (1H, OH), 10.12 s (2H, NH_2). Found, %: C 58.37; H 5.54; N 19.50. $C_{14}H_{16}N_4O_3$. Calculated, %: C 58.32; H 5.59; N 19.43.

2-[5-Amino-4-cyano-2-(ethylideneaminooxy)-2-phenylfuran-3(2*H*)-ylidene]malononitrile (IVa). A solution of 2.46 g (0.01 mol) of cyclopropane **IIa** in 10 ml of acetonitrile was added under stirring to a solution of 0.46 g (0.02 mol) of sodium in 10 ml of acetaldehyde oxime. The mixture was kept for 24 h, neutralized with 5% sulfuric acid, and extracted with ethyl acetate. The organic phase was dried over calcined sodium sulfate, the solvent was distilled off, and the residue was ground with 10 ml of water. The precipitate was filtered off and washed with water. Yield 1.92 g (63%), mp 143–144°C (decomp.). IR spectrum, ν, cm^{-1}: 3255, 3189 (NH_2); 2219 (C≡N); 1688 (C=C). ^1H NMR spectrum, δ, ppm: 1.98 d (3H, CH_3), 7.52 m (5H, C_6H_5), 8.00 q (1H, C**H**CH$_3$), 10.33 s and 10.37 s (2H, NH_2). Found, %: C 62.85; H 3.66; N 22.90. $C_{16}H_{11}N_5O_2$. Calculated, %: C 62.95; H 3.63; N 22.94.

Compounds **IVb**–**IVg** were synthesized in a similar way.

2-[5-Amino-2-(4-bromophenyl)-4-cyano-2-(ethylideneaminooxy)furan-3(2*H*)-ylidene]malononitrile (IVb). Yield 57%, mp 117–118°C (decomp.). IR spectrum, ν, cm^{-1}: 3233, 3090 (NH_2); 2216 (C≡N); 1693 (C=C). ^1H NMR spectrum, δ, ppm: 1.93 d (3H, CH_3), 7.50 d and 7.76 d (4H, C_6H_4), 8.01 q (1H, C**H**CH$_3$), 10.36 s and 10.42 s (2H, NH_2). Found, %: C 50.00; H 2.66; N 18.30. $C_{16}H_{10}BrN_5O_2$. Calculated, %: C 50.02; H 2.62; N 18.23.

2-[5-Amino-4-cyano-2-(ethylideneaminooxy)-2-(4-methoxyphenyl)furan-3(2*H*)-ylidene]malononitrile (IVc). Yield 72%, mp 181–182°C (decomp.). IR spectrum, ν, cm^{-1}: 3237, 3090 (NH_2); 2220 (C≡N); 1691 (C=C). ^1H NMR spectrum, δ, ppm: 1.93 d (3H, CH_3), 3.82 s (3H, OCH_3), 7.05 d and 7.48 d (2H each, C_6H_4), 7.99 q (1H, C**H**CH$_3$), 10.29 s and 10.31 s (2H, NH_2). Mass spectrum: *m*/*z* 335 (I_{rel} = 10%). Found, %: C 60.80; H 3.96; N 20.90. $C_{17}H_{13}N_5O_3$. Calculated, %: C 60.89; H 3.91; N 20.89.

2-[5-Amino-4-cyano-2-(ethylideneaminooxy)-2-(3,4-dimethoxyphenyl)furan-3(2*H*)-ylidene]malononitrile (IVd). Yield 61%, mp 162–163°C (decomp.). IR spectrum, ν, cm^{-1}: 3281, 3198 (NH_2); 2210 (C≡N); 1682 (C=C). ^1H NMR spectrum, δ, ppm: 1.93 d (3H, CH_3); 3.78 s and 3.80 s (3H each, OCH_3); 7.02 d, 7.04 s, and 7.08 d (3H, C_6H_3); 8.00 q (1H, C**H**CH$_3$); 10.28 s and 10.30 s (2H, NH_2). Found, %: C 59.25; H 4.16; N 19.20. $C_{18}H_{15}N_5O_4$. Calculated, %: C 59.18; H 4.14; N 19.17.

2-[5-Amino-4-cyano-2-(ethylideneaminooxy)-2-methylfuran-3(2*H*)-ylidene]malononitrile (IVe). Yield 78%, mp 207–208°C (decomp.). IR spectrum, ν, cm^{-1}: 3251, 3199 (NH_2); 2220 (C≡N); 1669 (C=C). ^1H NMR spectrum, δ, ppm: 1.85 d (3H, CHC**H**$_3$), 1.88 s (3H, CH_3), 7.75 q (1H, C**H**CH$_3$), 10.29 s (2H, NH_2). Mass spectrum: *m*/*z* 243 (I_{rel} 20%). Found, %: C 54.25; H 3.76; N 28.80. $C_{11}H_9N_5O_2$. Calculated, %: C 54.32; H 3.73; N 28.79.

2-[5-Amino-2-*tert*-butyl-4-cyano-2-(ethylideneaminooxy)furan-3(2*H*)-ylidene]malononitrile (IVf). Yield 76%, mp 228–229°C (decomp.). IR spectrum, ν, cm^{-1}: 3271, 3121 (NH_2); 2213 (C≡N); 1689 (C=C). ^1H NMR spectrum, δ, ppm: 1.02 m (9H, *t*-Bu), 1.91 d (3H, CHC**H**$_3$), 7.30 q (1H, C**H**CH$_3$), 10.08 s and 10.15 s (2H, NH_2). Mass spectrum: *m*/*z* 285 (I_{rel} = 5%). Found, %: C 58.85; H 5.36; N 24.60. $C_{14}H_{15}N_5O_2$. Calculated, %: C 58.94; H 5.30; N 24.55.

2-[5-Amino-4-cyano-2-(ethylideneaminooxy)-2-(2-thienyl)furan-3(2*H*)-ylidene]malononitrile (IVg). Yield 69%, mp 122–123°C (decomp.). IR spectrum, ν, cm^{-1}: 3256, 3174 (NH_2); 2203 (C≡N); 1682 (C=C). ^1H NMR spectrum, δ, ppm: 1.92 d (3H, CH_3); 7.14 t, 7.41 d, and 7.82 d (3H, C_4H_3S); 7.93 q (1H, C**H**CH$_3$), 10.35 s and 10.38 s (2H, NH_2). Found, %: C 54.05; H 2.96; N 22.60. $C_{14}H_9N_5O_2S$. Calculated, %: C 54.01; H 2.91; N 22.50.

2-[5-Amino-4-cyano-2-(isopropylideneaminooxy)-2-phenylfuran-3(2*H*)-ylidene]malononitrile (IVh). Metallic sodium, 0.46 g (0.02 mol), was dissolved on slight heating in a mixture of 2.92 g (0.04 mol) of acetone oxime and 10 ml of *tert*-butyl alcohol, and a solution of 2.46 g (0.01 mol) of cyclopropane **IIa** in 10 ml of acetonitrile was added under stirring. The mixture was kept for 24 h, neutralized

with 5% sulfuric acid, and extracted with ethyl acetate. The organic phase was dried over calcined sodium sulfate, the solvent was distilled off, and the residue was ground with 10 ml of water. The precipitate was filtered off and washed with water. Yield 2.87 g (90%), mp 234–235°C (decomp.). IR spectrum, ν, cm^{-1}: 3247, 3099 (NH_2); 2216 (C≡N); 1688 (C=C). ^1H NMR spectrum, δ, ppm: 1.97 s and 2.09 s (3H each, CH_3), 7.50–7.56 m (5H, C_6H_5), 10.30 s (2H, NH_2). Found, %: C 63.83; H 4.16; N 21.90. $C_{17}H_{13}N_5O_2$. Calculated, %: C 63.94; H 4.10; N 21.93.

Compounds **IVi–IVn** were synthesized in a similar way.

2-[5-Amino-2-(4-bromophenyl)-4-cyano-2-(isopropylideneaminooxy)furan-3(2*H*)-ylidene]malononitrile (IVi). Yield 76%, mp 215–216°C (decomp.). IR spectrum, ν, cm^{-1}: 3272, 3128 (NH_2); 2214 (C≡N); 1682 (C=C). ^1H NMR spectrum, δ, ppm: 1.95 s and 2.08 s (6H, CH_3), 7.52 d and 7.72 d (2H each, C_6H_4), 10.35 s (2H, NH_2). Found, %: C 51.25; H 3.17; N 17.50. $C_{17}H_{12}BrN_5O_2$. Calculated, %: C 51.27; H 3.04; N 17.59.

2-[5-Amino-4-cyano-2-(isopropylideneaminooxy)furan-3(2*H*)-ylidene]malononitrile (IVj). Yield 66%, mp 166–167°C (decomp.). IR spectrum, ν, cm^{-1}: 3256, 3104 (NH_2); 2214 (C≡N); 1687 (C=C). ^1H NMR spectrum, δ, ppm: 1.93 s and 2.08 s (3H each, CH_3), 3.80 s (3H, OCH_3), 7.03 d and 7.47 d (2H each, C_6H_4), 10.23 s (2H, NH_2). Found, %: C 61.85; H 4.36; N 20.12. $C_{18}H_{15}N_5O_3$. Calculated, %: C 61.89; H 4.33; N 20.05.

2-[5-Amino-4-cyano-2-(3,4-dimethoxyphenyl)-2-(isopropylideneaminooxy]furan-3(2*H*)-ylidene]-malononitrile (IVk). Yield 19%, mp 157–158°C (decomp.). IR spectrum, ν, cm^{-1}: 3279, 3164 (NH_2); 2208 (C≡N); 1684 (C=C). ^1H NMR spectrum, δ, ppm: 1.96 s and 2.08 s (3H each, CH_3); 3.78 s and 3.80 s (3H each, OCH_3); 7.04 d, 7.05 s, and 7.07 d (3H, C_6H_3); 10.21 s (2H, NH_2). Found, %: C 60.21; H 4.58; N 18.35. $C_{19}H_{17}N_5O_4$. Calculated, %: C 60.15; H 4.52; N 18.46.

2-[5-Amino-4-cyano-2-(isopropylideneaminooxy)-2-(3-nitrophenyl)furan-3(2*H*)-ylidene]malononitrile (IVl). Yield 63%, mp 220–221°C (decomp.). IR spectrum, ν, cm^{-1}: 3230, 3074 (NH_2); 2218 (C≡N); 1694 (C=C). ^1H NMR spectrum, δ, ppm: 1.99 s and 2.50 s (3H each, CH_3); 7.84 t, 8.04 d, 8.32 s, and 8.42 d (4H, C_6H_4); 10.46 s (2H, NH_2). Found, %: C 56.15; H 3.35; N 23.03. $C_{17}H_{12}N_6O_4$. Calculated, %: C 56.05; H 3.32; N 23.07.

2-[5-Amino-4-cyano-2-(isopropylideneaminooxy)-2-methylfuran-3(2*H*)-ylidene]malononitrile (IVm). Yield 73%, mp 228–229°C (decomp.); published data [16]: mp 230–235°C (decomp.).

2-[5-Amino-4-cyano-2-(isopropylideneaminooxy)-2-(2-thienyl)furan-3(2*H*)-ylidene]malononitrile (IVn). Yield 64%, mp 191–192°C (decomp.). IR spectrum, ν, cm^{-1}: 3271, 3150 (NH_2); 2218 (C≡N); 1685 (C=C). ^1H NMR spectrum, δ, ppm: 1.95 s and 2.03 s (3H each, CH_3); 7.15 t, 7.39 d, and 7.82 d (3H, C_4H_3S); 10.32 s (2H, NH_2). Found, %: C 55.35; H 3.46; N 21.60. $C_{15}H_{11}N_5O_2S$. Calculated, %: C 55.38; H 3.41; N 21.53.

Sodium 2-benzoyl-1,1,3,3-tetracyanopropenide (Va). A solution of 0.82 g (0.01 mol) of sodium acetate in 5 ml of water was added under stirring to a solution of 2.46 g (0.01 mol) of cyclopropane **IIa** in 10 ml of acetonitrile, and the mixture was stirred until the reaction was complete (according to the TLC data). The solution was evaporated to dryness, and the crystalline residue was washed with dioxane and recrystallized from aqueous isopropyl alcohol (1:1). Yield 2.39 g (89%), mp 228–229°C (decomp.). IR spectrum, ν, cm^{-1}: 2205 (C≡N), 1655 (C=O).

Compounds **Vb–Vh** were synthesized in a similar way.

Sodium 2-(4-bromobenzoyl)-1,1,3,3-tetracyanopropenide (Vb). Yield 91%, mp 221–222°C (decomp.). IR spectrum, ν, cm^{-1}: 2205 (C≡N), 1681 (C=O).

Sodium 1,1,3,3-tetracyano-2-(4-methoxybenzoyl)propenide (Vc). Yield 92%, mp 223–224°C (decomp.). IR spectrum, ν, cm^{-1}: 2200 (C≡N), 1664 (C=O).

Sodium 1,1,3,3-tetracyano-2-(3,4-dimethoxybenzoyl)propenide (Vd). Yield 90%, mp 186–187°C (decomp.). IR spectrum, ν, cm^{-1}: 2226 (C≡N), 1661 (C=O).

Sodium 1,1,3,3-tetracyano-2-(3-nitrobenzoyl)-propenide (Ve). Yield 90%, mp 213–214°C (decomp.). IR spectrum, ν, cm^{-1}: 2230 (C≡N), 1656 (C=O).

Ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide (Vf). Yield 86%, mp 181–182°C (decomp.). IR spectrum, ν, cm^{-1}: 3257, 3155, 3067 (NH_4^+); 2192 (C≡N); 1659 (C=O).

Crystallographic parameters: a = 8.1856(11), b = 9.5361(12), c = 10.1685(11) Å; α = 115.957(13), β =

102.087(12), γ = 103.220(12)°; V = 649.88(19) Å^3; Z = 2; space group $P1$. Total number of reflections 2531; number of reflections with $I > 2\sigma(I)$ 2233; number of refined parameters 218; divergence factor R = 0.038.

Sodium 1,1,3,3-tetracyano-2-(2,2-dimethyl-1-oxopropyl)propenide (Vg). *a*. The procedure was analogous to that described above for compound **Va**. Yield 89%, mp 206–207°C (decomp.). IR spectrum, ν, cm^{-1}: 2206 (C≡N), 1678 (C=O).

b. Metallic sodium, 0.46 g (0.02 mol), was dissolved on slight heating in a mixture of 2.92 g (0.04 mol) of acetone oxime and 10 ml of dioxane. The resulting solution was added under stirring to a suspension of 2.26 g (0.01 mol) of cyclopropane **IIg** in 10 ml dioxane. After some time, the precipitate was filtered off and washed with water. Yield 87%, mp 206–207°C (decomp.).

Sodium 1,1,3,3-tetracyano-2-(2-thienylcarbonyl)-propenide (Vh). Yield 93%, mp 183–184°C (decomp.). IR spectrum, ν, cm^{-1}: 2205 (C≡N), 1633 (C=O).

4-Amino-6-benzoyl-2,2-bis(isopropylideneaminooxy)-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitrile (VIa). Acetone oxime, 1.46 g (0.02 mol), was added under stirring to a solution of 2.46 g (0.01 mol) of cyclopropane **IIa** in 10 ml of acetonitrile. After 24 h, the precipitate was filtered off and washed with several portions of acetonitrile and water. Yield 2.43 g (62%), mp 195–196°C (decomp.). IR spectrum, ν, cm^{-1}: 3358, 3262 (NH_2); 3063 (C–H); 2246 (C≡N); 1668 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.75 s, 1.85 s, 1.87 s, and 1.98 s (3H each, CH_3); 4.09 s (1H, CH); 7.56 s (2H, NH_2); 7.59 t, 7.75 t, and 7.99 d (5H, C_6H_5). Found, %: C 61.25; H 5.26; N 21.30. $C_{20}H_{20}N_6O_3$. Calculated, %: C 61.21; H 5.14; N 21.42.

Compounds **VIb**–**VIe** were synthesized in a similar way.

4-Amino-2,2-bis(isopropylideneaminooxy)-6-(4-methoxybenzoyl)-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitrile (VIb). Yield (65%), mp 182–183°C (decomp.). IR spectrum, ν, cm^{-1}: 3348, 3269 (NH_2); 3069 (C–H); 2246 (C≡N); 1674 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.77 s, 1.85 s, 1.87 s, and 1.98 s (3H each, CH_3); 3.79 s (3H, OCH_3); 4.01 s (1H, CH); 7.10 d and 7.97 d (2H each, C_6H_4); 7.54 s (2H, NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.95, 21.45, 21.75 (CH_3); 34.42 (C^5); 38.86 (C^1); 41.14 (C^6); 55.90 (OCH_3); 111.93, 112.94 (CN); 114.29, 127.87, 131.39, 160.91 (C_6H_4); 123.17 (C^2); 158.26, 157.21 (N=C); 164.46 (C^4); 186.97 (C=O). Found, %: C 59.83; H 5.22; N 19.95. $C_{21}H_{22}N_6O_4$. Calculated, %: C 59.71; H 5.25; N 19.89.

4-Amino-6-(3,4-dimethoxybenzoyl)-2,2-bis(isopropylideneaminooxy)-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitrile (VIc). Yield 58%, mp 186–187°C (decomp.). IR spectrum, ν, cm^{-1}: 3342, 3252 (NH_2); 3075 (C–H); 2243 (C≡N); 1673 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.76 s, 1.86 s, 1.87 s, and 1.96 s (3H each, CH_3); 3.83 s and 3.89 s (3H each, OCH_3); 4.05 s (1H, CH); 7.11 d, 7.49 s, and 7.67 d (3H, C_6H_3); 7.53 s (2H, NH_2). Found, %: C 58.36; H 5.23; N 17.62. $C_{22}H_{24}N_6O_5$. Calculated, %: C 58.40; H 5.35; N 18.57.

4-Amino-2,2-bis(isopropylideneaminooxy)-6-(2,2-dimethyl-1-oxopropyl)-3-azabicyclo[3.1.0]-hex-3-ene-1,5-dicarbonitrile (VId). Yield (73%), mp 180–181°C (decomp.). IR spectrum, ν, cm^{-1}: 3332, 3266 (NH_2); 3077 (C–H); 2247 (C≡N); 1672 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.14 s (9H, *t*-Bu); 1.83 s, 1.85 s, 1.86 s, and 1.87 s (3H each, CH_3); 3.39 s (1H, CH); 7.48 s (2H, NH_2). Found, %: C 58.25; H 6.56; N 22.61. $C_{18}H_{24}N_6O_3$. Calculated, %: C 58.05; H 6.50; N 22.57.

Crystallographic parameters: a = 10.1568(14), b = 12.8889(16), c = 15.8516(15) Å; α = 90.00, β = 100.65(2), γ = 90.00°; V = 2039.4(4) Å^3; Z = 4; space group $P2_1/c$. Total number of reflections 3595; number of reflections with $I > 2\sigma(I)$ 1504; number of refined parameters 264; divergence factor R = 0.075.

4-Amino-2,2-bis(isopropylideneaminooxy)-6-(2-thienylcarbonyl)-3-azabicyclo[3.1.0]hex-3-ene-1,5-dicarbonitrile (VIe). Yield 65%, mp 161–162°C (decomp.). IR spectrum, ν, cm^{-1}: 3378, 3266 (NH_2); 3045 (C–H); 2249 (C≡N); 1668 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.73 s, 1.86 s, 1.87 s, and 1.94 s (3H, CH_3); 4.01 s (1H, CH); 7.34 t, 8.09 d, and 8.22 d (3H, C_4H_3S); 7.54 s (2H, NH_2). Found, %: C 54.25; H 4.67; N 21.10. $C_{18}H_{18}N_6O_3S$. Calculated, %: C 54.26; H 4.55; N 21.09.

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