Electrocatalytic transformation of malononitrile and cycloalkylidenemalononitriles into spirotricyclic and spirotetracyclic compounds containing cyclopropane and pyrroline fragments

M. N. Elinson,[a] S. K. Fedukovich,[a] T. A. Zaimovskaya,[b] A. N. Vereshchagin,[a] and G. I. Nikishin[a]*

[a]*N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: elinson@ioc.ac.ru*

[b]*A. V. Topchiev Institutute of Petrochemical Synthesis of the Russian Academy of Sciences, 29 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 1230 2224. E-mail: zatan@ips.ac.ru*

Electrolysis of cycloalkylidenemalononitriles and malononitrile in MeOH in an undivided cell in the presence of the NaBr—NaOMe mediator system gives spirotricyclic compounds containing cyclopropane and pyrroline fragments in 50—77% yields. Spirobicyclic and spirotricyclic tetracyanocyclopropanes undergo electrolysis in alcohols to afford spirotricyclic and spirotetracyclic products containing cyclopropane and pyrroline fragments in 50—93% yields.

Key words: electrolysis, electrocatalytic transformation, cycloalkylidenemalononitriles, malononitrile, mediators, spirotricyclic compounds.

This work continues the series of studies dealing with electrochemical transformation of CH-acids such as malononitrile, cyanoacetic ester, and malonic ester into functionally substituted cyclopropanes using mediators, namely, alkali metal halides.[1—4] A previous publication[4] reported co-electrolysis of malononitrile with cycloalkylidenemalononitriles **1a—d**, **2a—c**, and **3a,b** in the presence of NaBr resulting in the synthesis of tetracyano-substituted spirobicyclic and spirotricyclic compounds **4a—d**, **5a—c**, and **6a**,**b**, containing a cyclopropane fragment (Scheme 1).

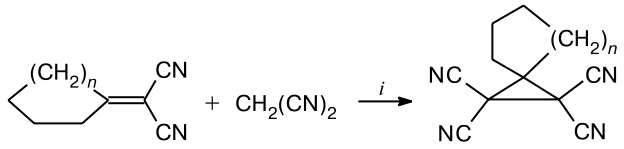
Here we report the results of a study dealing with electrocatalytic transformation of compounds **4a—d**, **5a—c**, and **6a**,**b** into bicyclic pyrrolines **7a—d**, **8a—c**, **9a**,**b**, and **10**. The reaction was carried out in an undivided cell under conditions similar to those used previously to perform electrocatalytic transformation of **4b** into **7b**[5] (Table 1, Scheme 2):

In all experiments, NaBr was used as the electrolyte and the quantity of electricity passed was 0.2 F mol^{-1}. The use of NaBr is not obligatory in this electrocatalytic process.

Similar results have been obtained using NaOAc and $LiNO_3$. Under the conditions studied, all bicyclic and tricyclic tetracyanocyclopropanes were converted into the corresponding tricyclic and tetracyclic pyrrolines in 50—95% yields.

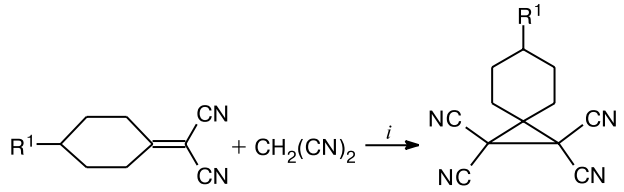
Pyrroline **8a** was isolated as a mixture of (*E*)- and (*Z*)- isomers in 4 : 1 ratio. In the case of pyrroline **8b**, the

Scheme 1



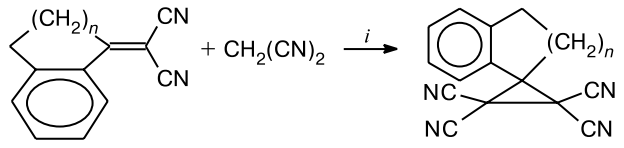
1a—d **4a—d**

n = 1 (**a**), 2 (**b**), 3 (**c**), 8 (**d**)



2a—c **5a—c**

R^1 = Me (**a**), R = Ph (**b**), Bu^t (**c**)



3a,b **6a,b**

n = 1 (**a**), 2 (**b**)

i. Electrolysis, NaBr, EtOH.

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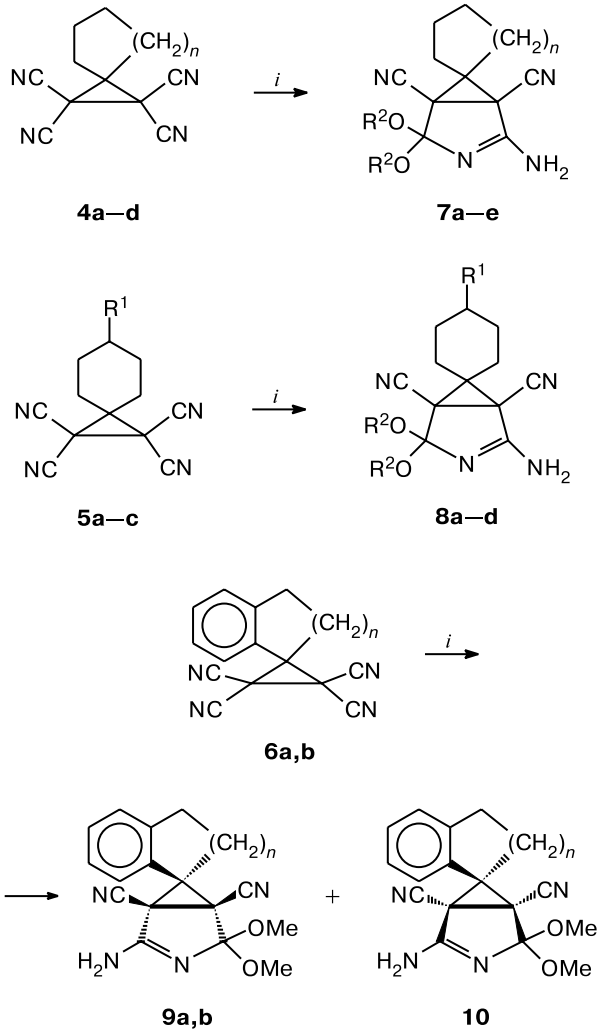
Scheme 2



6, 9: n = 1 (**a**), 2 (**b**)

Compound	**4** n	**5** R	**7** n	**7** R^2	**8** R^1	**8** R^2
a	1	Me	1	Me	Me	Me
b	2	Ph	2	Me	Ph	Me
c	3	Bu^t	2	Et	Bu^t	Me
d	8		3	Me	Bu^t	Et
e			8	Me		

i. Electrolysis, 0.2 F mol^{-1}, NaBr, R^2OH

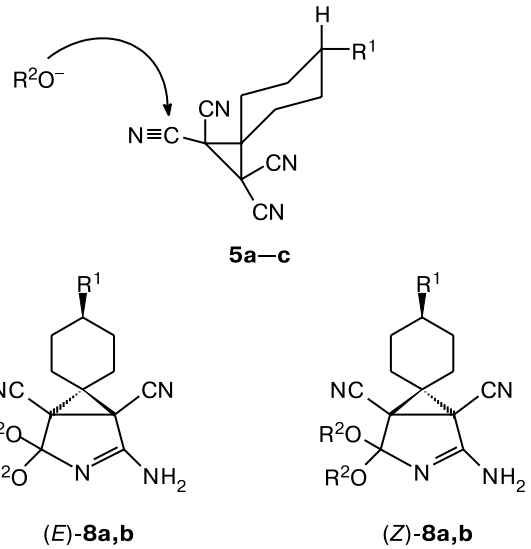
formation of a second isomer was also detected in the reaction mixture by NMR spectroscopy (the isomer ratio was 10 : 1).

In tetracyanocyclopropanes **5a—c**, the substituent R^1 is arranged predominantly in the equatorial position. Thus, the alkoxide ion attacks the sterically less hindered CN group linked to the equatorial C atom of the cyclopropane ring. This attack affords predominantly compounds (*E*)-**8a,b**, whereas in the case of **5c**, the reaction is

Table 1. Electrocatalytic transformation of bi- and tricyclic tetracyanocyclopropanes into tri- and tetracyclic pyrrolines[a]

Substrate	n	R^1	R^2	Pyrroline, yield (%)[b]
4a	1	—	Me	**7a**, 93
4b	2	—	Me	**7b**, 91
4b	2	—	Et	**7c**, 87
4c	3	—	Me	**7d**, 92
4d	8	—	Me	**7e**, 88
5a	—	Me	Me	**8a**, 51
5b	—	Ph	Me	**8b**, 57
5c	—	Bu^t	Me	**8c**, 89
5c	—	Bu^t	Et	**8d**, 83
6a	1	—	Me	**9a**, 65; **10**, 23
6b	2	—	—	**9b**, 75

[a] Conditions: 5 mmol of tetracyanocyclopropane, 5 mmol of NaBr, 20 mL of alcohol, undivided cell, Fe cathode, C anode, current density 20 mA cm^{-2}, quantity of electricity 0.2 F mol^{-1}, 20 °C.
[b] Relative to isolated pyrroline.

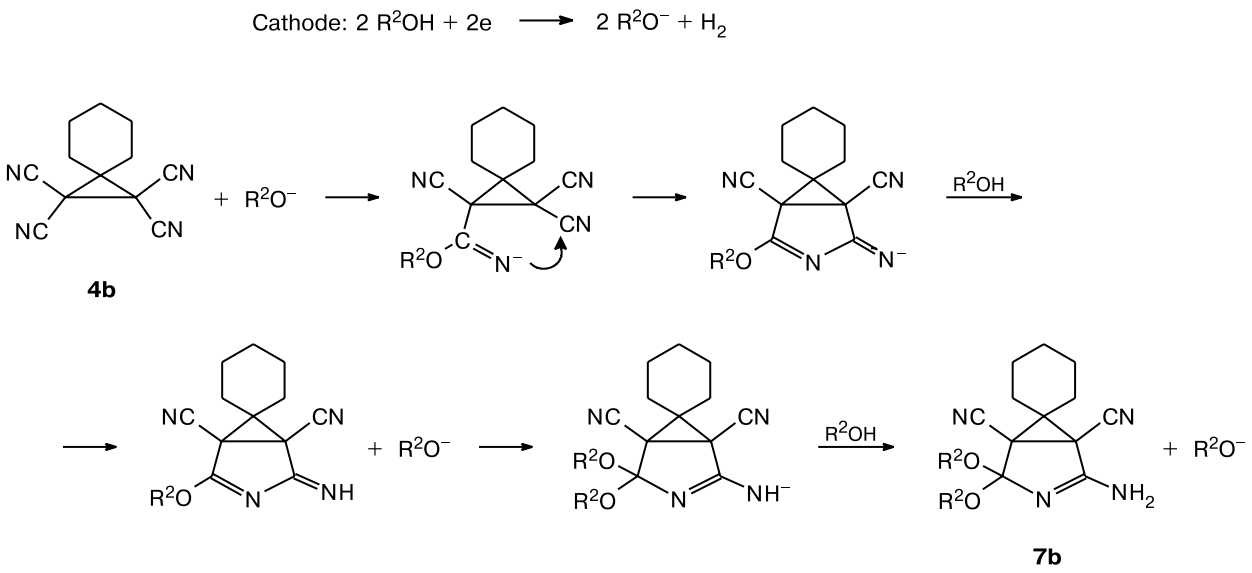


Compound	(*E*)-**8** **a**	**b**	**c**	**d**	(*Z*)-**8** **a**	**b**
R^1	Me	Ph	Bu^t	Bu^t	Me	Ph
R^2	Me	Me	Me	Et	Me	Me

stereoselective and gives (*E*)-**8c** or (*E*)-**8d** as the only product.

Electrocatalytic transformation of **6a** furnishes a mixture of isomeric pyrrolines **9a** and **10**. Pyrroline **9a** crystallizes directly from the reaction mixture, while pyrroline **10** was isolated by concentrating the mother liquor followed by extraction with chloroform and crystallization

Scheme 3



from MeOH. Compound **6b** was converted stereoselectively to give only pyrroline **9b** (Scheme 2). In view of the fact that a fused benzene ring creates steric hindrance to the attack of the CN group by the methoxide ion, structure **9** was proposed for the major isomers. A structure with the benzene and pyrroline rings arranged on the same side of the cyclopropane ring was proposed for isomers **10**.

As follows from the mechanism of the electrocatalytic process, generation of one methoxide anion is sufficient for this transformation. Scheme 3 shows this process in relation to electrocatalytic transformation of **4b** to **7b**.

Since the same inorganic salt, NaBr, is used as the mediator and the electrolyte in both the electrochemical transformation of malononitrile and cycloalkylidenemalononitriles **1a—d**, **2a—c**, **3a**,**b** into compounds **4a—d**, **5a—c**, and **6a**,**b**[4] and in the subsequent electrochemical preparation of pyrrolines from tetracyanocyclopropanes,[5] performing these reactions in one step as a cascade process according to the "domino" principle appeared to be the best choice.

However, it was found that, when the cascade process was carried out using 3 F mol^{-1} of electricity per mole of the starting alkylidenemalononitrile, the reaction mixture obtained after the electrolysis contained not only pyrrolines but also slight amounts of the intermediate tetracyanocyclopropanes. This circumstance decreases somewhat the yield of pyrrolines and hampers their isolation.

This drawback was eliminated by introducing an additional 0.1 equiv. of sodium alkoxide into the reaction system. As a result, in none of the experiments using equimolar amounts of cycloalkylidenemalononitrile and malononitrile, were the intermediate tetracyanocyclopropanes detected in the reaction mixture after electrolysis. Data on the direct transformation of malononitrile and cycloalkylidenemalononitriles **1a—d**, **2a—c**, and **3a**,**b** into tri- and tetracyclic pyrrolines are summarized in Table 2.

It follows from the data of Table 2 that in terms of the ability to be converted into the corresponding tricyclic and tetracyclic pyrrolines through electrolysis in the pres-

Table 2. Electrocatalytic transformation of malononitrile and cycloalkylidenemalononitriles into tri- and tetracyclic pyrrolines[a]

Substrate	n	R^1	R^2	Pyrroline, yield (%)[b]
1a	1	—	Me	**7a**, 66
1b	2	—	Me	**7b**, 77
1b[c]	2	—	Me	**7b**, 45
1c	3	—	Me	**7d**, 65
1d	8	—	Me	**7e**, 67
2a	—	Me	Me	**8a**, 53
2b	—	Ph	Me	**8b**, 57
2c	—	Bu^t	Me	**8c**, 51
3a	1	—	—	**9a**, 22; **10**, 9
3b	2	—	—	**9b**, 28

[a] Conditions: 10 mmol of malononitrile, 10 mmol of tetracyanocyclopropane, 5 mmol of NaBr, 1 mmol of RONa, 20 mL of alcohol, Fe cathode, C anode, current density 100 mA cm^{-2}, quantity of electricity 3 F mol^{-1}, 20 °C.

[b] Relative to isolated pyrroline. [c] A 1.5-fold excess of malononitrile; compound **4b** was identified in the reaction mixture by ^{1}H NMR spectroscopy, yield 19%.

ence of malononitrile, cycloalkylidenemalononitriles can be classified into three groups: (i) unsubstituted cycloalkylidenemalononitriles **1a—d** form pyrrolines **7a—d** in high yields (65—77%); (ii) substituted cyclohexylidenemalononitriles **2a—c** are converted into **8a—c** in good yields (51—57%); and (iii) benzoalkylidenemalononitriles **3a,b** are transformed into tetracyclic pyrrolines **9a**,**b** and **10** in 30% yield.

It has been shown previously that excess malononitrile prevents the transformation of tetracyanocyclopropanes into the corresponding pyrrolines.[4] When a 1.5-fold excess of malononitrile, instead of an equimolar amount, was introduced in the electrolysis under similar conditions, the yield of **7b** decreased from 77 to 45%.

However, efficient transformation of many cycloalkylidenemalononitriles into the corresponding tetracyanocyclopropanes with high product yields requires excess malononitrile, which becomes more pronounced with an increase in the bulk of substituents in cycloalkylidenemalononitrile.[4] Due to the presence of these two mutually exclusive conditions, direct transformation of cycloalkylidenemalononitriles into bicyclic pyrrolines in high yields occurs for unsubstituted cycloalkylidenemalononitriles **1a—d**. The presence of the substituent in **2a—c** diminishes the yield of **8a—c** to 50%. In the case of benzoalkylidenemalononitriles **3a,b**, the yield of the corresponding pyrrolines decreases to 30%.

The above results provided the grounds for proposing a mechanism for the joint electrochemical transformation of malononitrile and cycloalkylidenemalononitriles to give tricyclic and tetracyclic pyrrolines containing a cyclopropane fragment in one step.

The reactions that take place at the electrodes during the co-electrolysis of malononitrile and cycloalkylidenemalononitriles into tri- and tetracyclic pyrrolines containing a cyclopropane fragment are the usual reactions for the mediator system involved (bromide anion—molecular bromine), which include the formation of bromine at the anode and hydrogen evolution at the cathode with generation of alkoxide ions

$$\text{anode: } 2\,Br^- - 2e \longrightarrow Br_2,$$

$$\text{cathode: } 2\,ROH + 2e \longrightarrow 2\,RO^- + H_2.$$

The alkoxide ion reacts with malononitrile in the solution to give the malononitrile anion:

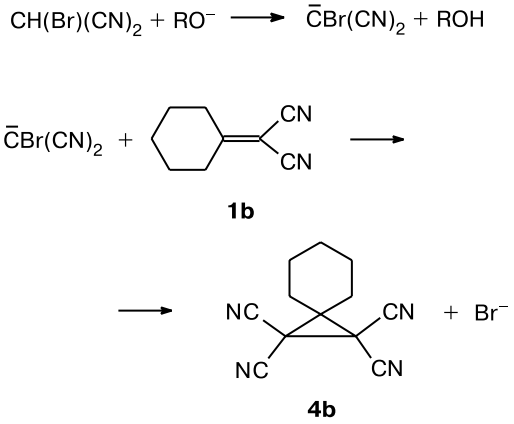
$$CH_2(CN)_2 + RO^- \longrightarrow \bar{C}H(CN)_2 + ROH.$$

The reaction of the malononitrile anion with bromine results in bromomalononitrile:

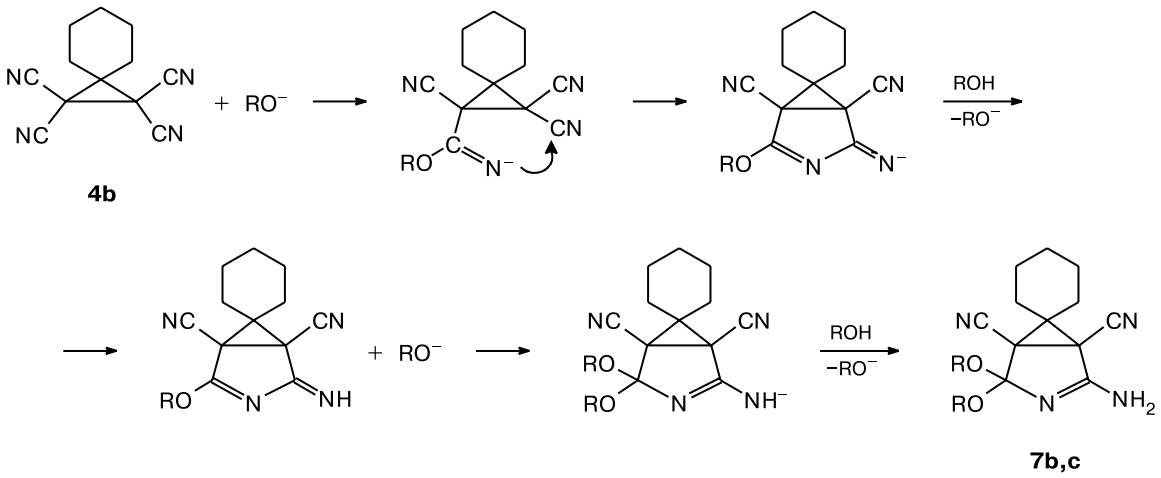
$$\bar{C}H(CN)_2 + Br_2 \longrightarrow CH(Br)(CN)_2 + Br^-.$$

The subsequent processes that take place in the solution are considered in relation to the co-electrolysis of malononitrile and cyclohexylidenemalononitrile **1b**.

Scheme 4



Scheme 5



R = Me (**b**), Et (**c**)

The bromomalononitrile anion generated under the action of the alkoxide ion adds to the double bond of nitrile **1b** to give cyclopropane **4b** (Scheme 4).

The subsequent reactions of cyclopropane **4b** with alkoxide ions result in the terminal compound in the cascade sequence, namely, tricyclic pyrroline **7b** or **7c** (Scheme 5).

Thus, we accomplished a cascade reaction proceeding according to the domino principle and permitting one-step synthesis of spirotricyclic and spirotetracyclic compounds containing cyclopropane and pyrroline fragments as co-electrolysis of malononitrile and cyclic alkylidenemalononitriles in an undivided cell in the presence of a mediator. Using techniques of classical organic chemistry, this transformation could be accomplished only as a three-step process comprising (i) halogenation of malononitrile, (ii) addition of halomalononitrile to the double bond of the cyclic alkylidenemalononitrile followed by cyclization,[6] (iii) reaction of the tetracyanocyclopropane obtained in step (ii) with alkoxide ions in alcohols.[4]

The electrochemical route we developed for the direct transformation of malononitrile and cyclic alkylidenemalononitriles into spirotricyclic and spirotetracyclic compounds containing a cyclopropane and a pyrroline fragment is convenient and economic; it makes use of common and readily available reagents, inexpensive equipment, and an undivided cell. The procedures of electrolysis and product isolation are facile and convenient when implemented both in the laboratory and on a pilot scale.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker WM-250 and Bruker AM-300 instruments operating at 250 and 300 MHz, respectively. The NMR chemical shifts are given in the δ scale and referred to Me_4Si. Malononitrile is a commercial preparation (Aldrich).

Cyclohexylidenemalononitriles **1a—d**, **2a—c,** and **3a,b** were prepared by Knövenagel condensation of the required ketones (commercial preparations, Merck and Aldrich) with malononitrile.[4,7]

Tetracyanocyclopropanes **4a—d**, **5a—c,** and **6a,b** were prepared by co-electrolysis of malononitrile and cyclohexylidenemalononitriles.[4]

Electrolysis of tetracyanocyclopropanes (general procedure). A solution of tetracyanocyclopropane (5 mmol) and NaBr (5 mmol) in 20 mL of an alcohol was electrolyzed in an undivided cell equipped with a C anode and a Fe cathode (the electrode area was 5 cm^2) at 20 °C and a constant current density equal to 20 mA cm^{-2}, while passing 0.2 F mol^{-1} of electricity. The precipitated pyrroline was filtered off and washed with cold alcohol. The reaction mixture was concentrated and extracted with acetone. The acetone was evaporated and the residue was crystallized from an acetone—hexane mixture to isolate an additional amount of pyrroline from the reaction mixture.

Co-electrolysis of malononitrile and cycloalkylidenemalononitriles (general procedure). A solution of malononitrile (10 mmol), cycloalkylidenemalononitrile (10 mmol), sodium alkoxide (1 mmol), and NaBr (5 mmol) in 20 mL of an alcohol was electrolyzed in an undivided cell equipped with a C anode and a Fe cathode (the electrode area was 5 cm^2) at 20 °C and a constant current density of 100 mA cm^{-2}, while passing 3 F mol^{-1} of electricity. The precipitated pyrroline was filtered off and washed with cold alcohol. The reaction mixture was concentrated and extracted with acetone. The acetone was evaporated and the residue was crystallized from an acetone—hexane mixture to isolate an additional amount of pyrroline from the reaction mixture.

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-tetramethylene-3-azabicyclo[3.1.0]hex-2-ene (7a), m.p. 214—216 °C (dec.). Found (%): C, 60.15; H, 6.07; N, 21.37. $C_{13}H_{16}N_4O_2$. Calculated (%): C, 59.99; H, 6.20; N, 21.52. ^{1}H NMR (DMSO-d_6), δ: 1.51 (m, 1 H); 1.69 (m, 5 H); 2.02 (m, 2 H); 3.26, 3.28 (both s, 3 H each, MeO); 7.32 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 24.8, 25.3, 27.2 (CH_2); 32.4 (CH_2); 39.2, 40.2, 49.0 (C); 48.9, 51.5 (OCH_3); 113.2, 114.6 (CN); 117.5 (O—C—O); 158.1 (C=N).

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-pentamethylene-3-azabicyclo[3.1.0]hex-2-ene (7b), m.p. 172—174 °C (dec.). Found (%): C, 61.14; H, 6.75; N, 20.27. $C_{14}H_{18}N_4O_2$. Calculated (%): C, 61.30; H, 6.61; N, 20.42. ^{1}H NMR (DMSO-d_6), δ: 1.47 (m, 2 H); 1.65 (m, 7 H); 1.97 (m, 1 H); 3.28, 3.30 (both s, 3 H each, MeO); 7.38 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 24.0, 24.4, 24.7, 25.5, 31.8 (CH_2); 39.3, 41.0, 45.0 (C); 48.8, 51.4 (OMe); 113.4, 114.4 (CN); 116.7 (O—C—O); 156.8 (C=N).

2-Amino-1,5-dicyano-4,4-diethoxy-6,6-pentamethylene-3-azabicyclo[3.1.0]hex-2-ene (7c), m.p. 155—156 °C (dec.) (Ref. 5: m.p. 155—157 °C (dec.)). ^{1}H NMR (DMSO-d_6), δ: 1.11, 1.14 (both t, 3 H each, J = 7 Hz); 1.40—2.05 (m, 10 H); 3.40—3.75 (m, 4 H, CH_2O); 7.40 (s, 2 H, NH_2).

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-hexamethylene-3-azabicyclo[3.1.0]hex-2-ene (7d), m.p. 128—130 °C. Found (%): C, 61.54; H, 6.85, N, 19.37. $C_{15}H_{20}N_4O_2$. Calculated (%): C, 62.48; H, 6.99; N, 19.43. ^{1}H NMR ($CDCl_3$), δ: 1.63 (m, 6 H); 1.85 (m, 4 H); 2.05 (m, 2 H); 3.38, 3.41 (both s, 3 H each, MeO); 5.95 (s, 2 H, NH_2). ^{13}C NMR ($CDCl_3$), δ: 24.2, 26.8, 27.9, 28.6, 35.2 (CH_2); 40.4, 41.9, 47.9 (C); 49.2, 51.9 (OMe); 112.7, 113.9 (CN); 116.6 (O—C—O); 157.8 (C=N).

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-undecamethylene-3-azabicyclo[3.1.0]hex-2-ene (7e), m.p. 130—132 °C (dec.). Found (%): C, 66.87; H, 8.35; N, 15.37. $C_{20}H_{30}N_4O_2$. Calculated (%): C, 67.01; H, 8.44; N, 15.63. ^{1}H NMR (DMSO-d_6), δ: 1.40—1.85 (m, 21 H); 2.06 (m, 1 H); 3.29, 3.31 (both s, 3 H each, MeO); 7.54 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 19.4, 20.3, 21.2, 21.5, 21.8, 24.2, 25.6, 25.7, 29.0 all CH_2, 39.8, 41.1, 46.6 (C); 48.8, 51.3 (OMe); 112.5, 115.1 (CN); 116.8 (O—C—O); 157.0 (C=N).

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-[(3-methyl)pentamethylene]-3-azabicyclo[3.1.0]hex-2-ene was isolated as a mixture of two isomers, (*E*)- and (*Z*)-(**8a**) (*E* : *Z* = 4 : 1), m.p. 153—154 °C (dec.). Found (%): C, 62.24; H, 6.85; N, 19.21. $C_{15}H_{20}N_4O_2$. Calculated (%): C, 62.48; H, 6.99; N, 19.43. ^{1}H NMR ($CDCl_3$), δ: 0.98 (m, 4 H); 1.27 (m, 1 H); 1.62 (m, 2 H); 1.85 (m, 4 H); 2.09 (m, 1 H); 3.34 and 3.35 ((*E*)-**8a**), 3.49 and 3.50 ((*Z*)-**8a**) (all s, 6 H, OMe)); 5.95 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), (*E*)-**8a**, δ: 21.64 (Me); 25.3, 31.3, 32.0

(CH_2); 31.8 (CH_2); 32.7 (CH); 39.1, 40.1, 45.1 (C); 48.8 (OMe); 51.2 (OMe); 113.5 (CN); 114.3 (CN); 116.9 (O—C—O); 156.9 (C=N). ^{13}C NMR (DMSO-d_6), (*Z*)-**8a**, δ: 21.2 (Me); 24.2, 30.1, 32.0, 31.8 (CH_2); 32.7 (CH); 39.0, 39.7, 44.1 (C); 48.8, 51.6 (OMe); 113.3, 114.6 (CN); 116.9 (O—C—O); 156.9 (C=N).

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-[(3-phenyl)pentamethylene]-3-azabicyclo[3.1.0]hex-2-ene (8b) was isolated as a mixture of two isomers (*E* : *Z* = 10 : 1), m.p. 198—200 °C (dec.). Found (%): C, 68.29; H, 6.25; N, 15.71. $C_{20}H_{22}N_4O_2$. Calculated (%): C, 68.55; H, 6.33; N, 15.99. ^{1}H NMR (DMSO-d_6), *E*-**8b**, δ: 1.50, 1.62 (both m, 1 H each); 1.78 (m, 3 H); 1.93, 2.09, 2.25 (all m, 1 H each); 3.27 (s, 6 H, MeO); 7.15—7.35 (5 H, Ph); 7.45 (s, 2 H, NH_2). ^{1}H NMR (DMSO-d_6), (*Z*)-**8b**, δ: 3.45 (s, OMe). ^{13}C NMR (DMSO-d_6), δ, (*E*)-**8b**: 25.0, 31.1, 31.3 (CH_2); 31.4 (C); 32.0 (CH_2); 41.5 (CH); 43.6 (C); 48.9, 51.5 (OMe); 112.7 (CN); 114.5 (CN); 116.7 (O—C—O); 125.9, 126.3, 128.2, 145.2 (all Ph); 156.7 (C=N).

(*E*)-2-Amino-6,6-[(3-*tert*-butyl)pentamethylene]-1,5-dicyano-4,4-dimethoxy-3-azabicyclo[3.1.0]hex-2-ene (8c), m.p. 210—212 °C (dec.). Found (%): C, 65.39; H, 7.81; N, 16.73. $C_{18}H_{26}N_4O_2$. Calculated (%): C, 65.43; H, 7.93; N, 16.96. ^{1}H NMR (DMSO-d_6), δ: 0.87 (s, 9 H); 1.00—1.30 (m, 3 H); 1.60, 1.75 (both m, 2 H each); 1.90, 2.12 (m, 1 H each); 3.22, 3.23 (both s, 3 H, MeO each); 7.55 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 25.2, 25.3, 25.3 (CH_2); 27.4 (Me); 27.6 (CH_2); 32.3, 32.6, 40.0, 44.5 (C); 46.1 (CH); 49.1, 51.9 (OMe); 113.3, 115.1 (CN); 116.8 (O—C—O); 157.0 (C=N).

(*E*)-2-Amino-6,6-[(3-*tert*-butyl)pentamethylene]-1,5-dicyano-4,4-diethoxy-3-azabicyclo[3.1.0]hex-2-ene (8d), m.p. 170—172 °C. Found (%): C, 66.85; H, 8.31; N, 15.41. $C_{20}H_{30}N_4O_2$. Calculated (%): C, 67.01; H, 8.44; N, 15.63. ^{1}H NMR (DMSO-d_6), δ: 0.87 (s, 9 H); 1.00—1.30 (m, 9 H); 1.60, 1.75 (both m, 2 H each); 1.90, 2.10 (both m, 1 H each); 3.60 (m, 4 H, CH_2O); 7.45 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 15.0, 15.4 (Me); 25.1, 25.8, 26.1 (CH_2); 27.5 (Me); 27.6 (CH_2); 31.9, 32.2, 40.1, 45.2 (C); 46.8 (CH); 57.0, 59.4 (OCH_2); 114.0 (O—C—O); 114.5, 116.2 (CN); 156.6 (C=N).

***anti*-2-Amino-1,5-dicyano-4,4-dimethoxyspiro[3-azabicyclo[3.1.0]hex-2-ene-6,1′-2′,3′-dihydro-1*H*-indene] (9a)** crystallizes directly from the reaction mixture, m.p. 169—171 °C (dec.). Found (%): C, 66.04; H, 5.11; N, 17.87. $C_{17}H_{16}N_4O_2$. Calculated (%): C, 66.22; H, 5.23; N, 18.17. ^{1}H NMR (DMSO-d_6), δ: 2.11, 2.58 (both m, 1 H each); 3.03 (m, 2 H); 3.29, 3.31 (both s, 3 H each, OMe); 7.44 (m, 4 H, Ar); 7.55 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 27.3, 28.9 (CH_2); 38.6, 39.3 (C); 49.1, 51.4 (OMe); 51.8 (C); 112.3, 113.6 (CN); 118.5 (O—C—O); 123.1, 125.2, 126.3, 129.4, 134.5, 146.4 (all Ar); 158.0 (C=N).

***syn*-2-Amino-1,5-dicyano-4,4-dimethoxyspiro[3-azabicyclo[3.1.0]hex-2-ene-6,1′-2′,3′-dihydro-1*H*-indene] (10)** was isolated by extraction with $CHCl_3$ of the residue remaining after evaporation of MeOH from the reaction mixture and crystallized from MeOH, m.p. 160—161 °C (dec.). Found (%): C, 66.09; H, 5.16; N, 17.96. $C_{17}H_{16}N_4O_2$. Calculated (%): C, 66.22; H, 5.23; N, 18.17. ^{1}H NMR (DMSO-d_6), δ: 2.31, 2.63 (both m, 1 H each); 3.05 (m, 2 H); 3.18, 3.33 (both s, 3 H each, OMe); 7.44 (m, 4 H, Ar); 7.53 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 28.5, 34.8 (CH_2); 38.4, 40.8 (C); 49.0 (OMe); 51.4 (C); 51.2 (OMe); 112.9, 114.3 (CN); 117.2 (O—C—O); 123.2, 124.7, 126.2, 129.3, 133.0, 147.0 (all Ar); 156.1 (C=N).

***anti*-2-Amino-1,5-dicyano-4,4-dimethoxyspiro[3-azabicyclo[3.1.0]-hex-2-ene-6,1′-1′,2′,3′,4′-tetrahydronapthalene] (9b)**, m.p. 160—162 °C (dec.). Found (%): C, 67.15; H, 5.41; N, 17.23. $C_{18}H_{18}N_4O_2$. Calculated (%): C, 67.07; H, 5.63; N, 17.38. ^{1}H NMR (DMSO-d_6), δ: 1.75, 1.84 (both m, 1 H each); 2.01, 2.89 (both m, 2 H each); 3.36, 3.38 (both s, 3 H each, OMe); 7.33 (m, 4 H, Ar); 7.60 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 19.8 (CH_2); 22.7 (C); 24.3, 28.7, 38.4 (CH_2); 44.9, 48.9 (C); 49.2, 51.3 (OCH_2); 113.0, 114.2 (CN); 118.5 (OCO); 124.9, 125.1, 128.2, 128.8, 131.1, 140.5 (all Ar); 157.5 (C=N).

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