The easy hydrolysis of hexacyanocyclopropane, ethyl 1,2,2,3,3-pentacyanocyclopropane-1-carboxylate, 1,2,2,3,3-pentacyanocyclopropane-1-carboxamide, and *N*,*N*-dimethyl-1,2,2,3,3-pentacyanocyclopropane-1-carboxamide to *r*-1,*c*-2,*c*-3-tricyanocyclopropane-*t*-carboxamide

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Hydrolysis of hexacyanocyclopropane (**1a**), ethyl 1,2,2,3,3-pentacyanocyclopropane-1-carboxylate (**1b**), 1,2,2,3,3-pentacyanocylopropane-1-carboxamide (**1c**), and *N*,*N*-dimethyl-1,2,2,3,3-pentacyanocylopropane-1-carboxamide (**1d**) in 95% acetic acid yields *r*-1,*c*-2,*c*-3-tricyanocyclopropane-*t*-1-carboxamide (**3**). The structure of **3** was proved by X-ray diffraction analysis.

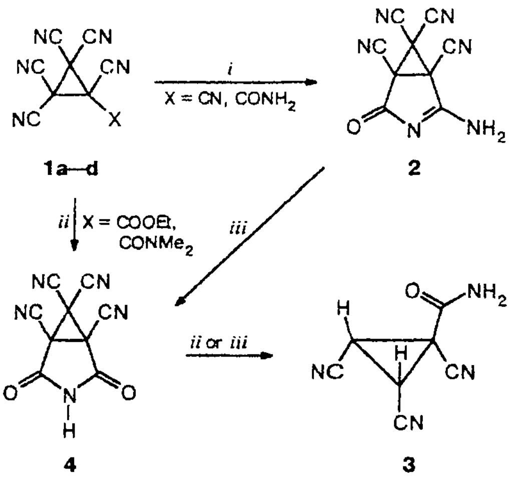
Key words: hexacyanocyclopropane, ethyl 1,2,2,3,3-pentacyanocyclopropane-1-carboxylate, 1,2,2,3,3-pentacyanocyclopropane-1-carboxamide, *N*,*N*-dimethyl-1,2,2,3,3-pentacyanocyclopropane-1-carboxamide, hydrolysis, *r*-1,*c*-2,c-3-tricyanocyclopropane-*t*-1-carboxamide, X-ray diffraction study.

Recently[1,2] we have shown that hexacyanocyclopropane (**1a**) readily reacts with methanol and ketoximes to give products of addition at the cyano groups, while the reaction of **1a** with aldoximes yields 2-amino-4-oxo-3-azabicyclo[3.1.0]hex-2-ene-1,5,6,6-tetracarbonitrile (**2**) (Scheme 1). The attempt to synthesize **2** directly by treatment of **1a** with water afforded unexpectedly *r*-1,*c*-2,*c*-3-tricyanocyclopropane-*t*-1-carboxamide (**3**). This unusual hydrolysis proceeds most smoothly when acetic acid is used in the presence of diethylamine or methanol. We found that under similar conditions, ethyl 1,2,2,3,3-pentacyanocyclopropane-1-carboxylate (**1b**), 1,2,2,3,3-pentacyanocyclopropane-1-carboxamide (**1c**), and *N*,*N*-dimethyl-1,2,2,3,3-pentacyanocyclopropane-1-carboxamide (**1d**) are also converted into compound **3**. The structure of product **3** was confirmed by X-ray diffraction analysis of its single crystal (Fig. 1).

These results suggest that the synthesis of compound **3** involves in all cases the same intermediate, namely, 2,4-dioxo-3-azabicyclo[3.1.0]hexan-1,5,6,6-tetracarbonitrile (**4**). In fact, this intermediate, obtained by the hydrolysis of compound **2** in the presence of sulfuric acid, is converted into compound **3** in aqueous AcOH in the presence of diethylamine. Compound **4** was also isolated as a product of hydrolysis of **1b** and **1c**.

The subsequent hydrolysis of **4** might result in the formation of amino acid **A**[3] (Scheme 2). Since acid **A** contains a cyano group in the vicinal position to the carbamoyl group, it undergoes cyclization giving a new pyrroline ring. Hydrolysis of the resulting bicyclic com-

Scheme 1



1a—d. X = CN (**a**), COOEt (**b**), CONH$_2$ (**c**), CONMe$_2$ (**d**)
i. RCH=NOH, met. Na, 35—40 °C, dioxane;[2]
ii. 95% AcOH + Et$_2$NH, 60 °C; *iii.* a solution of H$_2$SO$_4$ in aqueous alcohol, 60 °C.

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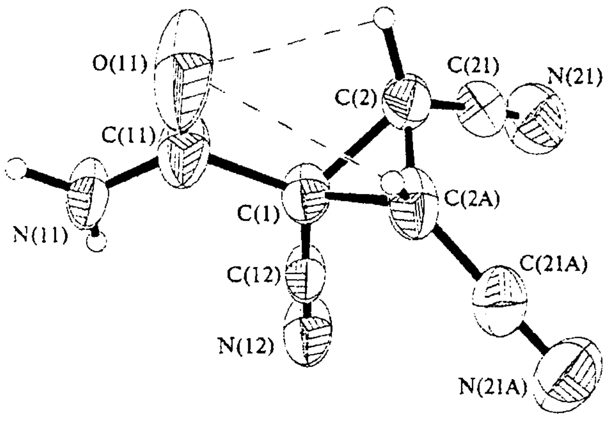
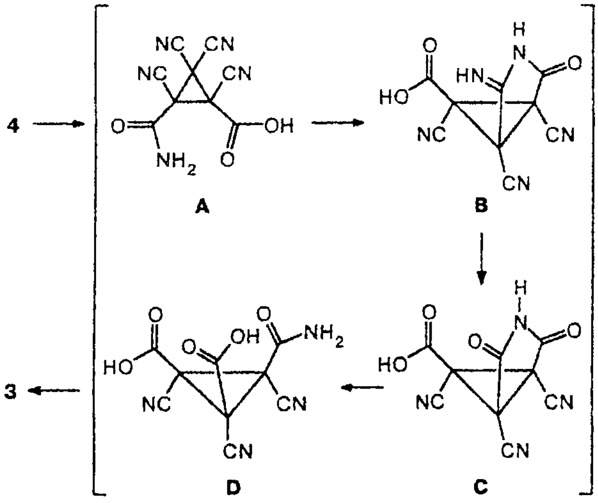


Fig. 1. Structure of the molecule of *r*-1,*c*-2,*c*-3-tricyanocyclopropane-*t*-1-carboxamide (**3**) with ellipsoids for the thermal vibrations of atoms; the dashed lines denote weak hydrogen bonds.

pound **B** and decarboxylation occurring *via* several intermediate steps, which presumably involve formation of intermediates **C** and **D**, finally lead to amide **3**. The formation of the latter compound from compounds **1a—d** and **4** is apparently due to the additional stabilizing interactions in molecule **3** caused by the formation of intramolecular hydrogen bonds between the oxygen atom of the carbamoyl group and the hydrogen atoms of the cyclopropane ring (see Fig. 1), which is indicated by the X-ray diffraction data (the O(11)···H(2) and O(11)···H(2a) distances are 2.48 (2) Å).

Scheme 2



Experimental

IR spectra were recorded on a UR-20 instrument in Vaseline oil. The purity of the synthesized compounds and the degree of completion of the reactions were determined by TLC (Silufol UV-254). Compounds **1b—d** were prepared by the procedure proposed for the synthesis of hexacyanocyclopropane (**1a**)[4] using monobromo derivatives of the corresponding methylene-active compounds instead of monobromomalononitrile.

***r*-1,*c*-2,*c*-3-Tricyanocyclopropane-*t*,1-carboxamide (3).** *A.* Hexanitrile **1a** (0.36 g, 1.9 mmol) was added in one portion to a mixture of 2 mL of MeOH and 3 mL of 95% AcOH. The mixture was stirred until the reagent completely dissolved. The resulting reaction mixture was allowed to stand in an open vessel for 3 days at ~20 °C. The resulting crystals were filtered off, washed with isopropyl alcohol, and dried over concentrated H_2SO_4 to a constant weight. Yield 0.1 g (32%), m.p. (decomp.) > 159 °C. Found (%): C, 52.47; H, 2.45; N, 34.97. $C_7H_4N_4O$. Calculated (%): C, 52.50; H, 2.50; N, 35.00. IR/cm^{-1}: 2270, 2280 (νC≡N); 3040 (νC—H); 3280, 3335, 3420 (νNH_2); 1710, 1670, 1590 (νC=O, δNH_2). Amide **3** was also obtained in a similar way from compounds **1b** and **1c** in 25 and 36% yields, respectively.

B. Sulfuric acid (0.11 g, 1 mmol) was dissolved in a mixture of 1 mL of distilled water and 1 mL of Pr^{i}OH; then compound **2** (0.42 g, 2 mmol) was added in portions. The mixture was heated on a water bath to 60 °C until **2** completely dissolved and allowed to stand at ~20 °C for 12 h. The precipitated crystals were filtered off and washed with Pr^{i}OH. Recrystallization from 1,4-dioxane gave 0.17 g (53%) of compound **3**.

C. Diethylamine (0.01 mL) was added in two portions to a suspension of imide **4** (0.2 g, 1 mmol) in 2 mL of 95% AcOH. The mixture was heated to 60 °C and stirred until **4** completely dissolved, then it was allowed to stand at ~20 °C for 4 days. The precipitated crystals were filtered off, washed with Pr^{i}OH, and dried over concentrated H_2SO_4 to a constant weight. Yield 0.04 g (25%). Amide **3** was also obtained in a similar way from compounds **1a—d** in 31, 25, 38, and 25% yields, respectively.

2,4-Dioxo-3-azabicyclo[3.1.0]hexane-1,5,6,6-tetracarbonitrile (4). *A.* 95% H_2SO_4 0.39 g (4 mmol) was dissolved in a mixture of 1 mL of distilled water and 1 mL of Pr^{i}OH, and cyanide **2** (0.21 g, 1 mmol) was added in portions. The mixture was heated on a water bath to 60 °C; during heating, the solution thickened, and precipitation of white crystals started. After keeping the mixture at ~20 °C for 15 h, the precipitate was filtered off, washed with Pr^{i}OH, and recrystallized from 1,4-dioxane to give 0.07 g (33%) of **4**, m.p. >135 °C (decomp.). Found (%): C, 51.00; H, 0.30; N, 33.00.

Table 1. Coordinates (×10^4, or ×10^3 for H) and isotropic (for nonhydrogen atoms, equivalent) thermal parameters (×10^3) of the atoms in the structure of **3**

Atom	*x*	*y*	*z*	*U*
O(11)	10295(3)	7500	3580(3)	123(2)
N(11)	8261(3)	7500	2241(3)	52(1)
N(12)	5599(3)	7500	5270(3)	60(1)
N(21)	7498(3)	5527(3)	8663(3)	72(1)
C(1)	8284(3)	7500	5157(3)	41(1)
C(11)	9027(3)	7500	3552(4)	59(1)
C(12)	6779(3)	7500	5199(3)	40(1)
C(2)	9025(2)	6724(3)	6506(2)	45(1)
C(21)	8189(3)	6025(3)	7702(3)	50(1)
H(1N)	869(4)	750	131(5)	55(11)
H(2N)	738(5)	750	230(6)	85(15)
H(2)	990(3)	626(3)	616(3)	55(7)

Table 2. Bond lengths (*d*) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å
O(11)—C(11)	1.216(4)	C(1)—C(11)	1.511(4)
N(11)—C(11)	1.313(4)	C(1)—C(2)	1.524(3)
N(12)—C(12)	1.133(4)	C(2)—C(21)	1.444(3)
N(21)—C(21)	1.143(3)	C(2)—C(2)*	1.503(5)
C(1)—C(12)	1.444(4)		

* *x*, −*y* + 3/2, *z*

Table 3. Bond angles (ω) in the structure of **3**

Angle	ω/deg	Angle	ω/deg
C(12)—C(1)—C(11)	119.6(3)	N(11)—C(11)—C(1)	117.8(3)
C(12)—C(1)—C(2)	116.6(2)	N(12)—C(12)—C(1)	178.4(3)
C(11)—C(1)—C(2)	115.3(2)	C(21)—C(2)—C(2)*	118.0(1)
C(2)*—C(1)—C(2)	59.1(2)	C(21)—C(2)—C(1)	118.5(2)
O(11)—C(11)—N(11)	125.1(3)	C(2)*—C(2)—C(1)	60.4(1)
O(11)—C(11)—C(1)	117.1(3)	N(21)—C(21)—C(2)	176.9(3)

* *x*, −*y* + 3/2, *z*.

$C_9HN_5O_2$. Calculated (%): C, 51.18; H, 0.47; N, 33.17. IR, ν/cm^{-1}: 2280 (C≡N); 1670, 1735, 1785 (C=O); 3375 (NH).

B. Diethylamine (0.01 mL) was added in two portions to a suspension of **1b** (0.3 g, 1.25 mmol) in 1.5 mL of 95% AcOH. The mixture was stirred at 50—60 °C until **1b** completely dissolved and kept at ~20 °C for two days, and the resulting crystals were filtered off, washed with Pr^iOH, and dried over H_2SO_4 to a constant weight to give 0.08 g (25%) of imide **4**. Imide **4** was obtained in 33% yield in a similar way from **1c**.

X-ray diffraction analysis of compound 3. The crystals of **3** are orthorhombic, space group *Pnma*; at 20 °C, a = 9.591(2), b = 9.683(2), c = 8.298(2) Å, V = 770.6(3) Å^3, Z = 4, d_{calc} = 1.380 g cm^{-3}, $C_7H_4N_4O$, M = 160.14. Unit cell parameters and the intensities of 727 reflections were measured on a Siemens P3/PC four-circle automatic diffractometer (20 °C, λMo-Kα, graphite monochromator, θ/2θ-scanning, θ_{max} = 25°). The structure was solved by the direct method and refined by full-matrix least squares in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms, localized objectively in a Fourier difference synthesis, were refined in the isotropic approximation. The final residual factors were R_1 = 0.048 over 511 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.126 over 698 independent reflections. All the calculations were carried out on an IBM PC/AT-486 using the SHELXTL PLUS and SHELXL-93 program packages. The coordinates and thermal parameters of the atoms and bond lengths and angles are presented in Tables 1—3.

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