

# Complexes of 2,6-Disubstituted 1-Oxa-4-thia-3,5-diazine 4,4-Dioxides with Symmetric Triazines as Supramolecular Systems. Preparation and Properties

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**Abstract**—Reactions of 2,6-disubstituted 1-oxa-4-thia-3,5-diazine 4,4-dioxides with substituted cyanamides in aromatic solvents (benzene, toluene, chlorobenzene, benzonitrile) furnished stable complexes including 1-oxa-4-thia-3,5-diazine 4,4-dioxide, symmetric triazine, and solvent (or no solvent) in a ratio 2 : 2 : 1. The molecules involved in the complexes are joined by intramolecular forces into a unified energetically favorable supramolecular system.

Recently a new line of investigations is intensively developed in organic chemistry corresponding to formation of stable multicomponent systems where the molecules or species are strongly linked by intramolecular forces (noncovalent interaction) into a unified system, a supramolecule. Therewith the properties of the arising supramolecular system sharply differ from those of its initial components [1–5].

The preparation of new structural forms of the supramolecular systems, the study of specific features of their structure and properties comprise an important goal of organic chemistry.

We recently demonstrated [6] that 2,6-disubstituted 1-oxa-4-thia-3,5-diazine 4,4-dioxides **I** readily reacted at 20°C with an equimolar amount of cyanamides yielding 2,4,6-trisubstituted 1-oxa-2-thia-3,5-diazine 2-oxides **II** [6].

The reaction of a representative of this class, 6-piperidino-2-trichloroacetyl-amino-4-trichloromethyl-1-oxa-2-thia-3,5-diazine 2-oxide (**II**, R = CCl<sub>3</sub>, R' = N-piperidyl) with cyanopiperidine in benzene provided a structural system **IIIa** built up of 2,4,6-tris(piperidino)-1,3,5-triazine, 2,6-bis-(trichloromethyl)-1-oxa-4-thia-3,5-diazine 4,4-dioxide, and benzene in a ratio 2:2:1. The structure of the crystalline supramolecule was determined by X-ray diffraction analysis [7] which revealed that in the crystal the separate molecules of dioxide **I**, triazine, and benzene are joined into structure **IIIa** by van der Waals forces.

The dioxide **I** and triazine rings in this system are present in the energetically feasible conformations: *semichair* and *chair* respectively [7].

In continuation of this research in order to extend the synthetic opportunities of complexes obtained, to reveal certain relations in the reaction conditions (the effect of substituents present in the rings of dioxide, oxide, and in the cyanamide) and the influence of the initial reagents ratio, and also to generalize the already existing information we studied the reactions of dioxides (**Ia**, R = CCl<sub>3</sub>; **Ib**, R = CBr<sub>3</sub>) with cyanamides (*N*-cyanopiperidine, *N*-cyanomorpholine, *N,N*-diethylcyanamide) in various solvents (C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Cl, C<sub>6</sub>H<sub>5</sub>CN, CHCl<sub>3</sub>, THF).

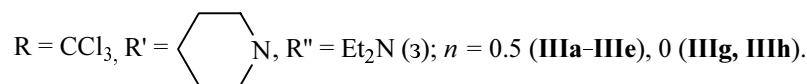
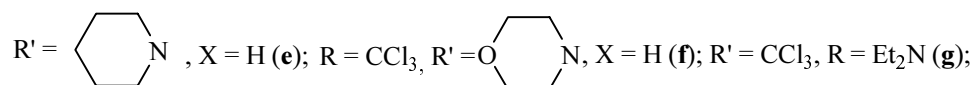
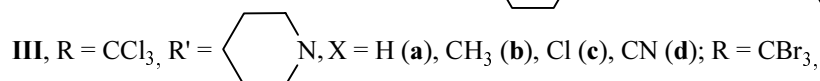
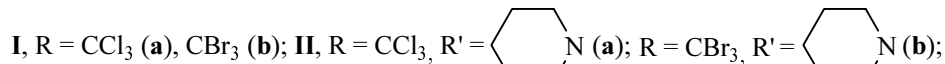
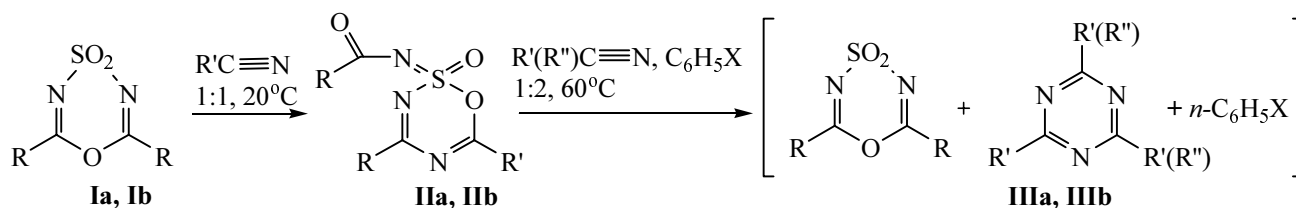
It was established that the reaction of dioxides **Ia** and **Ib** with *N*-cyanopiperidine and *N*-cyanomorpholine in a ratio 1:3 at 60°C in aromatic solvents (C<sub>6</sub>H<sub>5</sub>X, X = H, CH<sub>3</sub>, Cl, CN) gave rise to complexes **IIIa–IIIh** incorporating molecules of dioxide **Ia** or **Ib**, of the corresponding triazine, and of aromatic solvent (C<sub>6</sub>H<sub>5</sub>X) in a ratio 2:2:1. The complexes formed in reaction with diethylcyanamide **IIIg** and **IIIh** contained no solvent molecules.

Complexes **III** formed also in reactions of oxides **II** with cyanamides at the molar reagents ratio 1:2 [7]. Therefore the conversion of dioxides **I** and cyanamides into complex **III** may be represented by a stepwise process including formation of oxides **II** in the first stage followed by their reaction with cyanamide (Scheme 1).

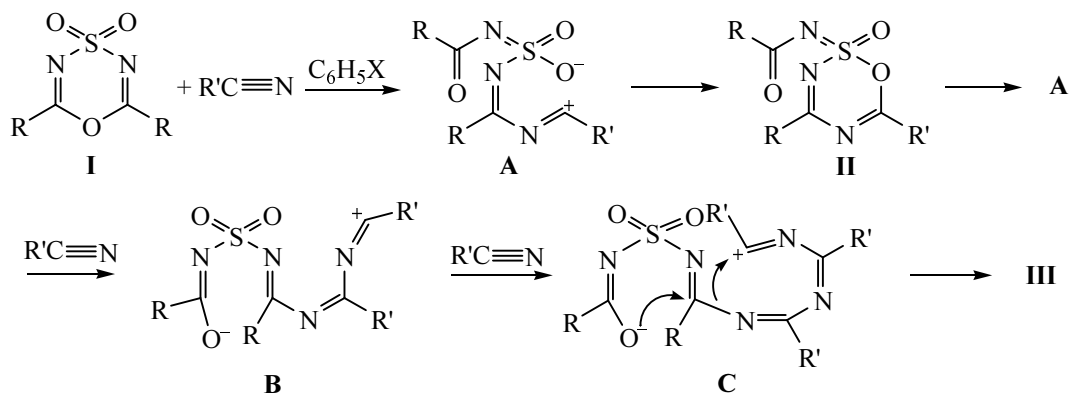
Actually, after heating dioxide **Ia** with excess cyanopiperidine (1:3) in benzene for 30 min at 60°C 18% of oxide **IIa** was found in the reaction mixture. In the parallel run at longer heating complex **IIIa** was obtained in a high yield. .

The reaction of dioxide **Ia** with excess diethylcyanamide at 60°C in benzene afforded complex **IIIg** contain-

Scheme 1.



Scheme 2.



ing dioxide **Ia** and 2,4,6-tris(diethylamino)-1,3,5-triazine in an equimolar ratio.

By performing a reaction of dioxide **Ia** with cyanopiperidine in benzene in a stepwise fashion (formation of oxide **IIa** in the first stage and reaction of the latter with diethylcyanamide in the second stage) we obtained complex **IIIh** containing dioxide **Ia** and 2,4,6-tris(diethylamino)-6-piperidino-1,3,5-triazine in an equimolar ratio. In the NMR spectra of complexes **IIIg** and **IIIh** the signals characteristic of benzene were lacking.

The composition and structure of supramolecules **IIIa-IIIh** were established from elemental analyses, IR,  $^1H$  NMR, and mass spectra. The structure of complex **IIIa** was determined by X-ray diffraction analysis [7].

The complexes **IIIa-IIIh** obtained are solid crystalline substances. They are more stable than the compounds contained in their composition. We failed to separate these substances into individual components. For instance, complex **IIIa** remained unchanged after heating at  $90^\circ C$  for 15 h in moist benzene, whereas dioxide **Ia** contained in this complex easily hydrolyzed at dissolution in cold water [8].

Complexes **III** in contrast to dioxide **I** do not react with cyanamides. After heating for 30 h at  $70^\circ C$  in chlorobenzene a mixture of complex **IIIc** and cyanopiperidine (1:2) the initial complex was recovered in 96% amount. Supramolecular systems **III** did not form at the use THF or  $CHCl_3$  as solvents. We also were not able to

prepare complexes **III** from the initial dioxides **I** and triazines.

From the data obtained here and published before [6, 7, 9] it is possible to suggest a probable scheme of the reaction route.

The formation of a strong supramolecular structure **III** owing to intermolecular forces is due to a good molecular concordance between dioxide **I** and the triazine arising in the course of the reaction (Scheme 2).

The key structure of this process is oxide **II**. It is presumable that its transformation in reaction with cyanamide into complex **III** involves formation of intermediates **A–C**. The molecules of dioxide **I** and triazine in the configurations corresponding to the intermolecular approach are formed in a concerted process (bond C–N rupture and C–O and C–N bonds formation) within intermediate **C**.

Apparently the solvent molecules (C<sub>6</sub>H<sub>5</sub>X) in the supramolecule **III** fill in the voids present in the structure. This role in reaction of dioxide **Ia** with diethylcyanamide in benzene is likely played by C<sub>2</sub>H<sub>5</sub> groups, and therefore in compounds **IIIg** and **IIIh** obtained benzene molecules are lacking.

## EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 80-M from solutions in CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR spectra were registered on a spectrometer Gemini 300 (operating frequency 300 MHz) from solutions in (CD<sub>3</sub>)<sub>2</sub>CO, internal reference TMS. Mass spectra were measured on MKh-1320 instrument, ionizing electrons energy 70 eV.

The homogeneity of compounds obtained was checked and the reaction progress was monitored by TLC on Silufol UV-254 plates, eluent acetone–hexane, 1:1 by volume, development in iodine vapor. The crystallization of complexes **IIIa–IIIh** obtained was performed from benzene.

**Complex IIIa.** To a solution of 1.00 g (2.71 mmol) of dioxide **Ia** in 20 ml of benzene was added at stirring 0.89 g (8.13 mmol) of *N*-cyanopiperidine in 5 ml of benzene. The reaction mixture was heated for 6 h at 60°C. The solvent was distilled off. The residue was treated with a mixture hexane–ether, 2:1 (10×5 ml). We obtained 1.80 g (90%) of complex **IIIa**, mp 150°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1185, 1385 (SO<sub>2</sub>), 1625, 1725 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.50–1.65 m [18H, 3(CH<sub>2</sub>)<sub>3</sub>], 3.60–3.85 t [12H, 3(CH<sub>2</sub>)<sub>2</sub>N], 7.33 s (3H, 0.5 C<sub>6</sub>H<sub>6</sub>).

Mass spectrum,  $m/z$ : 369 [ $M_1$ ]<sup>+</sup>, 330 [ $M_2$ ]<sup>+</sup>, 147 [CCl<sub>3</sub>CO]<sup>+</sup>, 110 [(CH<sub>2</sub>)<sub>5</sub>NCN]<sup>+</sup>, 84 [(CH<sub>2</sub>)<sub>5</sub>N]<sup>+</sup>, 78 [ $M_3$ ]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 64 [SO<sub>2</sub>]<sup>+</sup>, 36 [Cl]<sup>+</sup>. Found, %: C 40.60; H 4.55; Cl 29.14; N 15.51; S 4.30. C<sub>50</sub>H<sub>66</sub>Cl<sub>12</sub>N<sub>16</sub>O<sub>6</sub>S<sub>2</sub>. Calculated, %: C 40.64; H 4.50; Cl 28.86; N 15.65; S 4.34.

Likewise by reaction of dioxide **Ia** with *N*-cyanopiperidine in toluene, chlorobenzene, and benzonitrile were obtained complexes **IIIb–IIId** respectively.

**Complex IIIb.** Yield 87%, mp 151°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1175, 1375 (SO<sub>2</sub>), 1630, 1725 (C=N). Mass spectrum,  $m/z$ : 369 [ $M_1$ ]<sup>+</sup>, 330 [ $M_2$ ]<sup>+</sup>, 246 [ $M_2$ –NC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 147 [CCl<sub>3</sub>CO]<sup>+</sup>, 110 [(CH<sub>2</sub>)<sub>5</sub>NCN]<sup>+</sup>, 92 [ $M_3$ ]<sup>+</sup>, 84 [(CH<sub>2</sub>)<sub>5</sub>N]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 64 [SO<sub>2</sub>]<sup>+</sup>, 36 [Cl]<sup>+</sup>. Found, %: C 41.10; H 4.50; Cl 28.65; N 15.15; S 4.31. C<sub>51</sub>H<sub>68</sub>Cl<sub>12</sub>N<sub>16</sub>O<sub>6</sub>S<sub>2</sub>. Calculated, %: C 41.06; H 4.59; Cl 28.59; N 15.02; S 4.30.

**Complex IIIc.** Yield 86%, mp 149°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1170, 1365 (SO<sub>2</sub>), 1620, 1725 (C=N). Mass spectrum,  $m/z$ : 369 [ $M_1$ ]<sup>+</sup>, 330 [ $M_2$ ]<sup>+</sup>, 251 [ $M_1$ –CCl<sub>3</sub>]<sup>+</sup>, 246 [ $M_2$ –NC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 113 [ $M_3$ ]<sup>+</sup>, 110 [(CH<sub>2</sub>)<sub>5</sub>NCN]<sup>+</sup>, 84 [(CH<sub>2</sub>)<sub>5</sub>N]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 64 [SO<sub>2</sub>]<sup>+</sup>, 48 [SO], 36 [Cl]<sup>+</sup>. Found, %: C 39.75; H 4.37; Cl 30.50; N 14.87; S 4.20. C<sub>59</sub>H<sub>65</sub>Cl<sub>13</sub>N<sub>16</sub>O<sub>6</sub>S<sub>2</sub>. Calculated, %: C 39.71; H 4.33; Cl 30.55; N 14.82; S 4.24.

**Complex IIId.** Yield 82%, mp 139°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1160, 1355 (SO<sub>2</sub>), 1625, 1730, 2265 (C=N). Mass spectrum,  $m/z$ : 369 [ $M_1$ ]<sup>+</sup>, 330 [ $M_2$ ]<sup>+</sup>, 110 [(CH<sub>2</sub>)<sub>5</sub>NCN]<sup>+</sup>, 103 [ $M_3$ ]<sup>+</sup>, 84 [(CH<sub>2</sub>)<sub>5</sub>N]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 64 [SO<sub>2</sub>]<sup>+</sup>, 48 [SO], 36 [Cl]<sup>+</sup>. Found, %: C 40.70; H 4.41; Cl 28.12; N 15.79; S 4.30. C<sub>51</sub>H<sub>65</sub>Cl<sub>12</sub>N<sub>17</sub>O<sub>6</sub>S<sub>2</sub>. Calculated, %: C 40.76; H 4.36; Cl 28.38; N 15.84; S 4.27.

Under the similar conditions by reaction of dioxide **Ib** with *N*-cyanopiperidine in benzene was obtained **complex IIIe**. Yield 89%, mp 125°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1185, 1365 (SO<sub>2</sub>), 1635, 1730 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.45–1.75 m [18H, 3(CH<sub>2</sub>)<sub>3</sub>], 3.65–3.85 t [12H, 3(CH<sub>2</sub>)<sub>2</sub>N], 7.35 s (3H, 0.5 C<sub>6</sub>H<sub>6</sub>). Found, %: C 29.90; H 3.35; Br 47.74; N 11.10; S 3.20. C<sub>50</sub>H<sub>66</sub>Br<sub>12</sub>N<sub>16</sub>O<sub>6</sub>S<sub>2</sub>. Calculated, %: C 29.88; H 3.31; Br 47.70; N 11.15; S 3.19.

Complexes **IIIa–IIId** were also prepared by reacting oxide **IIa** with a twofold molar excess of *N*-cyanopiperidine at heating for 6–8 h to 60°C in benzene, toluene, chlorobenzene, and benzonitrile in yields 83, 85, 80, 75, and 88% respectively. Complex **IIIe** was obtained by reaction of oxide **IIb** with *N*-cyanopiperidine in benzene (60°C) in a 88% yield.

**Complex IIIf.** To a solution of 0.70 g (1.90 mmol) of dioxide **Ia** in 15 ml of benzene was added at stirring

0.66 g (5.89 mmol) of *N*-cyanomorpholine. The mixture was heated for 7 h at 60°C. The reaction mixture was treated with a saturated water solution of Na<sub>2</sub>CO<sub>3</sub> and then with water till neutral washings. The organic layer was dried over MgSO<sub>4</sub>, the solvent was distilled off, and the residue was treated with hexane (10×5 ml). We obtained 0.74 g (53%) of complex **III**f, mp 162°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1165, 1365 (SO<sub>2</sub>), 1635, 1725 (C=N). Mass spectrum,  $m/z$ : 369 [ $M_1$ ]<sup>+</sup>, 330 [ $M_2$ ]<sup>+</sup>, 112 [O(CH<sub>2</sub>)<sub>4</sub>NCN]<sup>+</sup>, 86 [O(CH<sub>2</sub>)<sub>4</sub>N]<sup>+</sup>, 78 [ $M_3$ ]<sup>+</sup>, 64 [SO<sub>2</sub>]<sup>+</sup>, 48 [SO], 36 [Cl]<sup>+</sup>. Found, %: C 35.46; H 3.68; Cl 28.70; N 15.00; S 4.32. C<sub>44</sub>H<sub>54</sub>Cl<sub>12</sub>N<sub>16</sub>O<sub>12</sub>S<sub>2</sub>. Calculated, %: C 35.48; H 3.65; Cl 28.63; N 15.04; S 4.30.

**Complex III**g. In 15 ml of benzene was dissolved 1.00 g (2.70 mmol) of dioxide **I**a, 0.86 g (8.64 mmol) of diethylcyanamide was added, and the mixture was heated for 9 h at 60°C. The solvent was distilled off, the residue was washed with hexane (10×7 ml) and ether (6×3 ml). We obtained 1.65 g (92%) of complex **III**g, mp 115°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1175, 1370 (SO<sub>2</sub>), 1635, 1745 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.12–1.43 t (18H, 6CH<sub>3</sub>), 3.45–3.70 m (12H, 6CH<sub>2</sub>). Mass spectrum,  $m/z$ : 369 [ $M_1$ ]<sup>+</sup>, 294 [ $M_2$ ]<sup>+</sup>, 196 [ $M_2 - (C_2H_5)_2NCN$ ]<sup>+</sup>, 147 [CCl<sub>3</sub>CO]<sup>+</sup>, 36 [Cl]<sup>+</sup>. Found, %: C 34.31; H 4.60; Cl 32.18; N 16.81; S 4.87. C<sub>19</sub>H<sub>30</sub>Cl<sub>6</sub>N<sub>8</sub>O<sub>3</sub>S. Calculated, %: C 34.38; H 4.56; Cl 32.13; N 16.88; S 4.83.

**Complex III**h. To a solution of 0.30 g (0.63 mmol) of oxide **I**a in 10 ml of benzene was added at stirring 0.13 g (1.32 mmol) of diethylcyanamide in 4 ml of benzene. The mixture was heated for 3 h at 60°C, the solvent was distilled off, the residue was treated with hexane (5×5 ml). We obtained 0.31 g (70%) of complex **III**h, mp 75°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1170, 1360 (SO<sub>2</sub>), 1625, 1635, 1730 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.10–1.35 t (12H, 4CH<sub>3</sub>), 1.60–1.80 m [6H, (CH<sub>2</sub>)<sub>3</sub>], 3.50–3.70 m [8H, 2(CH<sub>2</sub>)<sub>2</sub>N], 3.70–3.85 t [4H, (CH<sub>2</sub>)<sub>2</sub>N]. Found, %: C 35.60; H 4.45; Cl 31.61; N 16.62; S 4.71. C<sub>20</sub>H<sub>30</sub>Cl<sub>6</sub>N<sub>8</sub>O<sub>3</sub>S. Calculated, %: C 35.54; H 4.47; Cl 31.55; N 16.58; S 4.74.

In each of two ampules was first dissolved 1.00 g (2.71 mmol) of dioxide **I**a in 20 ml of benzene, then 0.89 g (8.13 mmol) of *N*-cyanopiperidine in 5 ml of benzene was added thereto. Both ampules were heated at 60°C. In 30 min from one ampule the solvent was distilled off, the residue was treated with a mixture hexane–ether, 2:1 (10×5 ml). Thus 0.24 g (18%) of oxide **I**a was obtained. In the parallel run the heating was continued for 5.5 h more, then the solvent was distilled off, the residue was treated with a mixture hexane–ether, 2:1, (10×5 ml) to isolate 1.80 g (90%) of complex **III**a.

To 0.50 g (0.34 mmol) of complex **III**a was added 25 ml of moist benzene, and the mixture was heated for 15 h at 90°C. The solvent was distilled off, the residue was washed with hexane (2×5 ml). We obtained 0.49 g (98%) of initial complex **III**a.

In 25 ml of hot (70°C) benzene was dissolved 0.50 g (0.33 mmol) of complex **III**c, 0.11 g (1.02 mmol) of *N*-cyanopiperidine was added, and heating at 70°C was continued for 30 h. The solvent was distilled off, the residue was washed with hexane (10×5 ml). We obtained 0.48 g (96%) of initial complex **III**c.

To a solution of 0.10 g (0.21 mmol) of oxide **I**a in 3.5 ml of THF was added 46 mg (0.42 mmol) of *N*-cyanopiperidine, and the mixture was heated at 55°C for 5 h. On removing the solvent we obtained 0.15 g of unidentified viscous substance.

To a solution of 0.15 g (0.32 mmol) of oxide **I**a in 5 ml of CHCl<sub>3</sub> was added 70 mg (0.64 mmol) of *N*-cyanopiperidine, and the mixture was heated at 50°C for 5 h. On removing the solvent we obtained 0.22 g of unidentified viscous substance.

To a solution of 0.14 g (0.42 mmol) of 2,4,6-tris-(piperidino)-1,3,5-triazine in 5 ml of benzene was added a solution of 0.16 g (0.42 mmol) of 2,6-bis(trichloromethyl)-1-oxa-4-thia-3,5-diazine-4,4-dioxide (**I**a) in 1.5 ml of benzene. The mixture was heated at 60°C for 3.5 h. The solvent was distilled off, the residue was treated with water (2×3 ml), and dried with ether. We isolated 0.11 g (78%) of unreacted *symm*-triazine.

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