

Synthesis of *endo,exo*-7,8,9,10-Tetrachlorobicyclo[4.4.0]deca-7,9-diene-3,4-dicarboxylic Acid *N,N'*-Bisimides

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Abstract—A one-stage synthesis was developed of *N,N'*-(3,3'-dimethoxy-4,4'-diphenylmethane)- and *N,N'*-(1,2-ethane)-*endo,exo*-7,8,9,10-tetrachlorobicyclo[4.4.0]deca-7,9-diene-3,4-dicarboxylic acids bisimides by reaction of a bisadduct of 1,8,9,10,11,11-hexachlorotricyclo[6.2.1.0^{5,10}]-undec-9-ene-4,5-dicarboxylic acid *N,N'*-R-bisimide with pyridine in DMF. The spatial structure of compounds obtained was established.

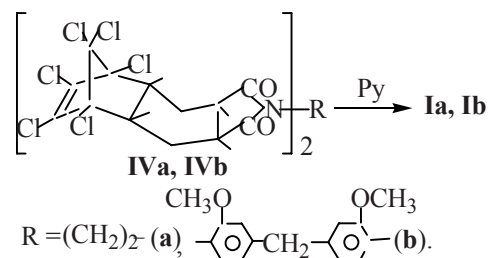
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Polymer materials endowed with high fire and heat resistance often contain in their molecules polychlorinated imide fragments [1, 2]. A great promise in this respect possess chlorinated *N*-substituted imides of cyclic dihydric acids [3, 4] that are used as monomers in the synthesis of incombustible polyimides. Especial interest is attracted by polychlorinated cyclic bisimido-dienes of dihydric acids employed in the polycondensation with bismaleimides in the preparation of polyimides by the stereospecific Diels–Alder reaction [5].

The synthesis of polychlorinated polycyclic dicarboxylic acids bisimidodienes was not described in the literature save [6] where a two-stage procedure was reported for the preparation of bisimidodiene **I** by acid hydrolysis of a diene adduct of *endo,exo*-1,8,9,10-tetrachloro-11,11-dimethoxytricyclo-[6.2.1.0^{5,10}]undec-9-ene-4,5-dicarboxylic acid *N,N'*-(1,2-ethane)bisimide (**II**) of a known spatial structure followed by a thermolysis of the isolated ketobisimide (**III**).

The goal of this study was the development of a one-stage synthesis of bisimidodienes based on polychlorinated

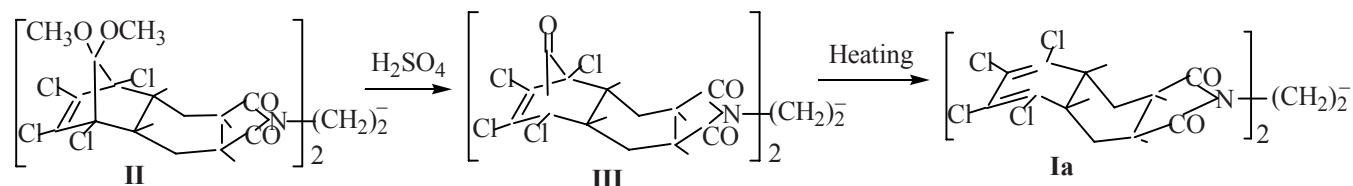
polycyclic dicarboxylic acids by a reaction of a diene adduct of 1,8,9,10,11,11-hexachlorotricyclo[6.2.1.0^{5,10}]-undec-9-ene-4,5-dicarboxylic acid *N,N'*-R-bisimides **IVa** and **IVb** with pyridine (Py) in dimethylformamide environment.



The characteristics of bisimidodiene **Ia** synthesized by the method we developed were completely identical to those of this compound obtained previously by the two-stage procedure [6].

The structure and composition of bisimidodienes **Ia** and **Ib** were proved by elemental analysis, molecular weight measurement, IR and UV spectra, and indepen-

Scheme 1.



dent syntheses. In the IR spectra absorption bands were observed in the region 1601, 1610 cm^{-1} (C=C bond), 1710–1780 cm^{-1} (C=O group), and 680–800 cm^{-1} (C–Cl bond). In the UV spectra of compounds **Ia** and **Ib** an adsorption band was observed with a maximum at 285–287 nm corresponding to the π - π^* transition and proving the presence of a diene chromophore.

Inasmuch as bisimidodienes **Ia** and **Ib** were obtained through the diene adducts **IVa** and **IVb** of the known structure with the *endo,exo*-configuration of the cyclohexane ring [7] the bisimidodienes **Ia** and **Ib** should have retained this configuration for the reaction performed did not involve the bonds at the rings junction.

The structure of compounds **Ia** and **Ib** was confirmed by an independent synthesis consisting in the acylation of anhydridodiene diamine **VI** that in its turn was obtained by the reaction of a diene adduct of *endo,exo*-1,8,9,10,11,11-hexachlorotricyclo[6.2.1.0^{5,10}]undec-9-ene-4,5-dicarboxylic acid anhydride (**V**) with pyridine in DMF.

The characteristics of bisimidodienes **Ia** and **Ib** obtained by any method were identical.

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer Specord M-80. UV spectra were registered on a Specord UV instrument from methanol solutions of concentration $3.0 \times 10^{-4} \text{ mol l}^{-1}$. The molecular weight was measured by cryoscopy.

endo,exo-1,8,9,10,11,11-Hexachlorotricyclo[6.2.1.0^{5,10}]undec-9-ene-4,5-dicarboxylic acid *N,N'*-bisimides **IVa** and **IVb** were obtained by procedure [8].

Bisimide **IVa**. Yield 91%, mp 183–185°C (benzene–hexane), R_f 0.61. IR spectrum, ν , cm^{-1} : 1600, 1608 (C=C),

1710, 1778 (C=O), 650–760 (C–Cl). Found, %: C 38.98; H 2.61; Cl 48.06; N 3.97. M 872. $\text{C}_{28}\text{H}_{20}\text{Cl}_{12}\text{N}_2\text{O}_4$. Calculated, %: C 38.44; H 2.28; Cl 48.74; N 3.20. M 874.

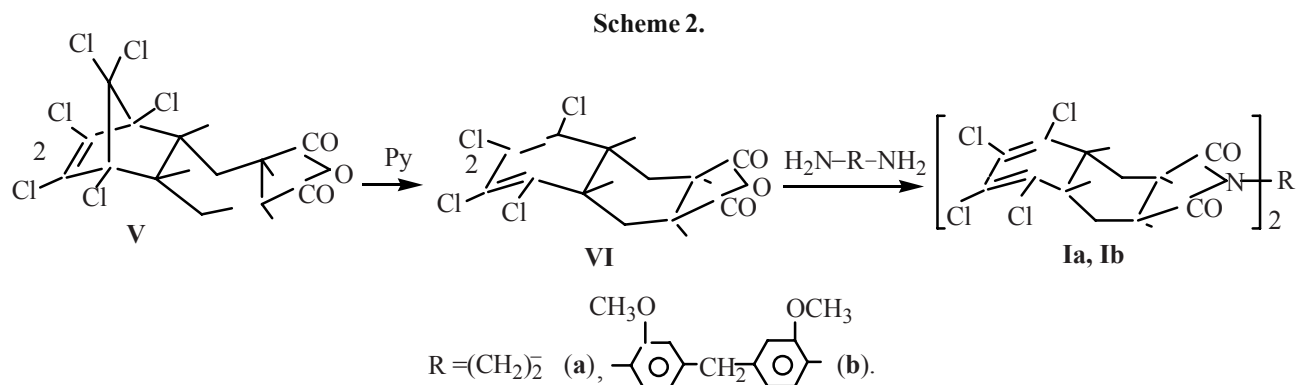
Bisimide (IVa). Yield 93%, mp 170–172°C (benzene–hexane), R_f 0.76. IR spectrum, ν , cm^{-1} : 1603, 1610 (C=C), 1716, 1780 (C=O), 660–780 (C–Cl). Found, %: C 45.72; H 3.08; Cl 39.11; N 2.91. M 1071. $\text{C}_{41}\text{H}_{30}\text{Cl}_{12}\text{N}_2\text{O}_6$. Calculated, %: C 45.89; H 2.79; Cl 39.74; N 2.61. M 1072.

1,8,9,10,11,11-Hexachlorotricyclo-[6.2.1.0^{5,10}]-undec-9-ene-4,5-dicarboxylic acid anhydride (V) was obtained by procedure [9]. mp 278°. Found, %: C 36.18; H 1.11; Cl 49.85. M 423. $\text{C}_{13}\text{H}_8\text{Cl}_6\text{O}_3$. Calculated, %: C 36.70; H 1.88; Cl 50.12. M 425.

7,8,9,10-Tetrachlorobicyclo[4.4.0]deca-7,9-diene-3,4-dicarboxylic acid anhydride (VI) was obtained by procedure [10]. mp 260°C. Found, %: C 41.89; H 2.00; Cl 40.91. M 343. $\text{C}_{12}\text{H}_8\text{Cl}_4\text{O}_3$. Calculated, %: C 42.10; H 2.34; Cl 41.52. M 342.

endo,exo-7,8,9,10-Tetrachloro-bicyclo-[4.4.0]-deca-7,9-diene-3,4-dicarboxylic acid *N,N'*-bisimides **Ia** and **Ib**. *a*. In 20 ml of DMF was dissolved 0.1 mol of bisimide **IVa** or **IVb** at room temperature, and to the solution was added dropwise 3 ml of pyridine. The mixture self-heated to 35°C. When the mixture cooled to 20°C it was poured at stirring into ice water. The separated crystals were filtered off and washed with water till neutral washings, then recrystallized, and dried.

b. In 100 ml of DMF was dissolved 0.2 mol of anhydridodiene **VI** and to the solution was added 0.1 mol of diamine. The mixture was heated at stirring to 120°C for 5 h. Then the reaction mixture was poured at stirring into ice water. The separated crystals were filtered off and repeatedly washed with water, dried, and recrystallized from a mixture benzene–hexane, 1:1.



Bisimidodiene Ia. Yield 80.0%, mp 223–226°C (benzene–hexane), R_f 0.71. IR spectrum, ν , cm^{-1} : 1601, 1610 (C=C), 1710, 1780 (C=O), 680–800 (C–Cl). Found, %: C 44.21; H 2.77; Cl 40.18; N 3.78. M 706. $\text{C}_{26}\text{H}_{20}\text{Cl}_8\text{N}_2\text{O}_4$. Calculated, %: C 44.06; H 2.82; Cl 40.11; N 3.95. M 708.

Bisimidodiene Ib. Yield 88.5%, mp 193–195°C (benzene–hexane), R_f 0.80. IR spectrum, ν , cm^{-1} : 1601, 1610 (C=C), 1710, 1780 (C=O), 660–780 (C–Cl). Found, %: C 50.89; H 3.00; Cl 31.77; N 2.99. M 905. $\text{C}_{39}\text{H}_{30}\text{Cl}_8\text{N}_2\text{O}_6$. Calculated, %: C 51.65; H 3.31; Cl 31.34; N 3.09. M 906.

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