SYNTHESIS AND STRUCTURE OF 9,10,11,12-DIBENZ[a,c]-7,14-DIAZA-1,4-DIOXACYCLOHEXADECANE-8,13-DIONE

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The reaction of diphenic acid dioxatriethylenediamide with a methanolic solution of amines leads to splitting of the imide heterocyclic ring by methanol with the formation of the corresponding amidoester of diphenic acid. Amines catalyze this reaction. 9,10,11,12-Dibenz[a,c]-7,14-diaza-1,4-dioxahexadecane-8,13-dione was obtained from diphenoyl dichloride and the corresponding diamine. An x-ray diffraction study has been carried out.

The reaction of polyoxyethylenediamines with polyoxyethylenediphthalimides leads to the formation of macrocyclic diamides, which cannot be obtained by the acid chloride method [1]. In the latter case N-substituted isoimides are formed [2, 3].

To clarify the possibility of the synthesis of a macrocyclic diamide from diphenic acid by the imide method, we carried out the reaction of 3,6-dioxaoctane-18-di(2,2'-diphenyldicarboximide) (I) with a methanolic solution of 3,6-dioxaoctane-1,8-diamine (II). Although the reaction of imides with alcoholic solutions of amines usually results in splitting of the imide heterocyclic ring with the formation of diamides, and not the alcoholysis [4], we obtained the corresponding amidoester of diphenyl-2,2'-dicarboxylic acid (III).

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\begin{align*}
\text{H}_2\text{N} & \quad \text{O} & \quad \text{NH}_2 \\
\text{O} & \quad \text{N} & \quad \text{O} \\
\text{MeO} & \quad \text{O} & \quad \text{MeO} \\
\text{HN} & \quad \text{O} & \quad \text{HN}
\end{align*}
\]

The reaction proceeds in the presence of butyl- and triethylamine, where the formation of diamides is in principle ruled out. This indicates that amines play a catalytic role, and also that the addition of stronger nucleophilic reagents is not always the preferential path of the reaction of imides.

The macrocyclic diamide — 9,10,11,12-dibenz[a,c]-7,14-diaza-1,4-dioxacyclohexadecane-8,13-dione (IV) — was obtained by the reaction of diphenoyl dichloride with diamine II under conditions described in [2], where the formation of isoimides is also possible.

In systems similar to IV, the conformational features of the ring are determined both by the rigid fragments (aromatic rings and the amide groups) and by the ring sizes [5-7].

To determine the steric structure of the macrocyclic compound IV and to discover the reasons for the formation of the macrocyclic 16-membered, and not the 7-membered mesocyclic isoimide system, we carried out an x-ray diffraction study of diamide IV. Its steric model is shown in Fig. 1 (the atom coordinates, the bond lengths between them, and the valence angles are given in Tables 1-3). The separate molecules in the crystal are joined by hydrogen bonds N(11)−H...O(25) = 2859 Å in the chain, and van der Waals interaction takes place between them. In the macrocyclic compound IV a fairly strained structure is realized. The strains in the molecules are caused by the small size of the ring preventing the occurrence of the C−H...O

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\text{IV}
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