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ЭКСПЕРТНОЕ ЗАКЛЮЧЕНИЕ О ВОЗМОЖНОСТИ ОПУБЛИКОВАНИЯ

Руководитель-эксперт Федерального государственного бюджетного учреждения науки Института элементоорганических соединений им. А.Н.Несмеянова Российской академии наук, рассмотрев *статью* авторов V.A. Karnoukhova, A.V. Vologzhanina, V.V. Baranov, A.N. Kravchenko, I.V. Fedyanin «**Self-organization of 1,6-dialkyl-3a,6a-dephenylglycolurils in the crystalline state**», подготовленную для печати в журнале CrystEngComm, подтверждает, что в материале *не содержатся* сведения, предусмотренные Постановлением Правительства РФ №1233 от 30.11.1994г. и на публикацию материала *не следует* получать разрешение *Минобрнауки и/или Президиума РАН*

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зав. лаб. Ю.В. Нелюбина

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ARTICLE

Self-organization of 1,6-dialkyl-3a,6a-diphenylglycolurils in the crystalline state

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Valentina A. Karnoukhova,[a] Vladimir V. Baranov,[b] Anna V. Vologzhanina,[a] Angelina N. Kravchenko[b,c] and Ivan V. Fedyanin[a,c]*

Peculiarities of self-organization of 1,6-dimethyl(diethyl)-3a,6a-diphenylglycolurils in crystals were studied. Glycolurils were synthesized and crystals of 16 solid forms (two pure substances, fourteen solvates) were obtained by crystallization from different solvents. The effect of solvent on dimensionality of H-bonding architectures and crystal morphology was revealed. The most widespread experimentally observed H-bonding synthon is the chain based on the amide-amide $R^2_2(8)$ motif, and solvent molecules typically act as terminal groups toward these chains. This is in accord with results of pairwise interaction energies calculation between glycolurils and glycoluril/solvent pairs. Parallel packing of these H-bonded chains in some cases results in crystal morphology facetted by hydrophobic alkyl and aryl moieties and provides materials with superhydrophobic surface. It was proposed that bulk water is repelled due to the corrugation of surfaces formed by the alkyl and aryl groups.

Introduction

Tetrahydroimidazo[4,5-*d*]imidazol-2,5(1*H*,3*H*)-diones, commonly known as glycolurils, as well as their derivatives have a long history and play an important role in organic and supramolecular chemistry[1–4]. They can be used as psychotropic agents[5,6], explosives[7], xerogels[8], anion receptors[9,10], galogenation reagents[11]. The concave shape of the molecules and the presence of multiple hydrogen bond donor and acceptor sites allow their application in supramolecular chemistry and crystal engineering as molecular capsules[4,12], bowls[13], and chiral hydrogen-bonded ribbons[14,15] obtained through the self-organization.

The majority of 1,6- and 1,4-disubstituted 3a,6a-diarylglycolurils studied to date form in the solid state hydrogen-bonded chains **A** and **B** via a H-bonded amide···amide $R^2_2(8)$ synthon (Fig. 1).

It is interesting that in the case of hydrocarbon substituents in 1,6- and 1,4-positions the external surface of the ribbons depicted in Fig. 1 is expected to be mainly hydrophobic. Indeed, for 1,6- and 1,4-dibenzyl-3a,6a-diphenylglycolurils[15] (Refcodes OHEKER and OHEKIV in the Cambridge Structural Database[16], CSD) both donors and acceptors of H-bonds are located *inside* the supramolecular architecture, while their surface is formed by hydrophobic aryl groups (Fig. 2). Other examples from CSD show that in general the hydrophobic character of the surface for chains **A** seems to be more expressed than for chains **B**. In either case, if hydrophobic chains pack parallel to each other and to faces of a crystal, materials with (super)hydrophobic surface can be obtained. For glycoluril derivatives, one can expect the formation of predictable 2D motifs constrained by H-bonds between the molecules of the neighbouring chains or, in the case of multicomponent crystals, through interactions with co-formers. This family of compounds can therefore provide a basis for developing clean hydrophobic surfaces for organic beam epitaxy[17].

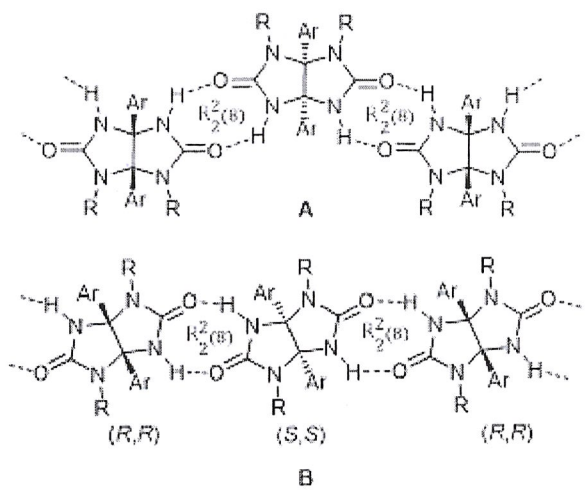

Fig. 1 Schematic representations of the chain structural motifs in 1,6-disubstituted 3a,6a-diarylglycolurils (**A**) and 1,4-disubstituted 3a,6a-diarylglycolurils (**B**)

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: octy@xrlab.ineos.ac.ru*
[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation, Fax: +7 499 135 5328; e-mail: ase1313@mail.ru.*
[c] *Plekhanov Russian University of Economics, Stremyanny lane 36, Moscow, 117997, Russian Federation.*

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Low-dimensional H-bonded architectures (dimers, chains, and layers) are connected through dispersion interactions so that this family of compounds exhibits prominent anisotropy of non-covalent interactions. Some of the solids obtained are facetted by low-energy surfaces with hydrophobic properties. We demonstrated for the first time that alkyl-substituted glycolurils can be used for the design of materials with superhydrophobic properties.

Conflicts of interest

There are no conflicts to declare.

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