



Design and supramolecular structure of crystal associates of polyfluoroarylenediamines and 18-crown-6 (2:1)

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ARTICLE INFO

Article history:

Received 12 September 2016

Received in revised form

28 November 2016

Accepted 28 November 2016

Available online 30 November 2016

Keywords:

Supramolecular associates

Polyfluorinated arylenediamines

18-crown-6

X-ray diffraction analysis

Crystal melting enthalpy

vdW-DFT calculations

ABSTRACT

The possibility of co-crystallization of polyfluoroaromatic *meta*-diamines with 18-crown-6 in the 2:1 ratio was tested using a large group of substrates with various frameworks (benzene, naphthalene, and pyridine) and substituents (H, Cl, CF₃). Co-crystals of 2:1 stoichiometry were obtained from hexafluoro-2,7-naphthylenediamine, 4-trifluoromethyltrifluoro- and 2-trifluoromethyl-4,6-difluoro-1,3-phenylene diamines, 4-chlorodifluoro-2,6-diaminopyridine. According to X-ray crystallographic data, associates of CF₃-containing polyfluorophenylenediamines are 2D assemblies connected via synthon C_{ar}-N-H ... O_{cr}. Polyfluorinated 2,7-diaminonaphthalene and 2,6-diamino-4-chloropyridine form 1D assemblies, in which the π -stacking of the naphthylenediamine molecules and the hydrogen bond C_{ar}-N-H ... N_{py}, respectively, are the additional structure-supporting interactions. The co-crystallization of 18-crown-6 with less electron withdrawing arylenediamines gives only associates of stoichiometry 1:1 irrespective of the components ratio and the solvent nature. To rationalize the different co-crystallization behavior of the arylenediamines, the co-crystal structures were studied using a special version of the DFT, which accounts for the van der Waals interactions. The calculated difference between the specific sublimation enthalpies for the 1:1 and 2:1 associates was suggested to be a measure of the preferable co-crystallization ratio: the both types of associates are formed when $|\Delta\Delta H^{\text{subl}}|$ is smaller than 15 J g⁻¹, a higher value indicates a significant energy preference for one of the structures. The experimental melting enthalpy values (DSC data) for the 1:1 and 2:1 co-crystals based on the same diamine are quite similar.

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1. Introduction

Crystal supramolecular associates formed via non-covalent interactions are of considerable interest due to their use in optoelectronics, electric conductivity, nonlinear optics, magnetism, and catalysis, as drug delivery tools and in a number of other applications [1–6]. The design of co-crystals with certain properties is based on the control of the architecture of a macroscale object at the molecular level [7–10], which is achieved by the efficient selection of the molecular components and by taking into account the

patterns of intermolecular interactions. For this reason, the study of the relationships between the supramolecular architecture of co-crystals, on the one hand, and the chemical structure of their components, on the other hand, is a subject of both material technology and fundamental science.

Previously, we studied the regularities of the architecture of a large group of co-crystals of 1:1 stoichiometry composed of 18-crown-6 ether and polyfluorinated *meta*-arylenediamines with a various framework (benzene, naphthalene and pyridine) modified with substituents of different nature, number, and mutual arrangement [11–14]. It was established that these co-crystals consisted of parallel 1D supramolecular assemblies (rods) with “arylenediamine-crown” as the repeating unit (Fig. 1). Structure of the 1D assemblies is supported by the only strong intermolecular

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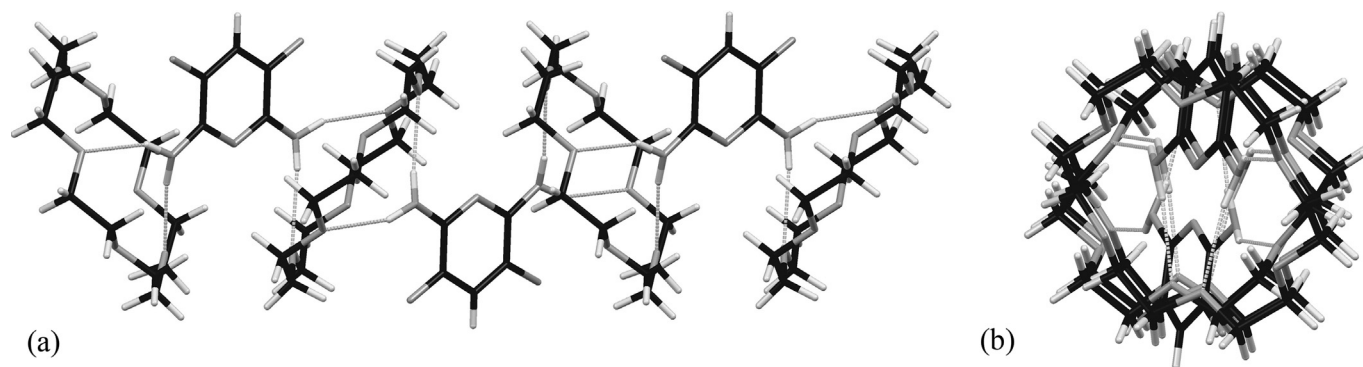


Fig. 1. Typical structure of the 1D assembly by example of the associate of 2,6-diamino-3,5-difluoropyridine with 18-crown-6: side (a) and cross-section (b) views (from Ref. [13]).

interaction, the H-bonded synthon $C_{ar}-N-H \dots O_{cr}$. In the series of the associates, there was found a relationship between the co-crystal melting enthalpy and the 1D assembly unit length [15]. This relationship underlies the selective co-crystallization of polyfluoroarylenediamines with crown ether (the molecular recognition principle) and was used in practice for the separation of isomeric arylenediamines and their isolation from monoamines [16–18].

It is obvious that the expansion of the types of synthons involved in the design of co-crystals leads to a greater diversity of their architecture, which should affect their functional properties. There are known examples of associates of crown ethers with amino compounds in which, along with the synthon $C_{ar}-N-H \dots O_{cr}$, other types of intermolecular bonding occur: $C = S \dots H-N-C_{aliph}$ in the associate with thiourea [19], $C_{ar}-N-CH_2-H \dots O_{cr}$ in the associate with methylthiourea [20], $O_{cr} \dots H^+-NH_2-C_{ar}$ in the associate with 3-aminoanilinium [21], and so on. A significant number of such associates are 2D and 3D structures. In some co-crystals of crown ethers with monoamino- and monohydrazinoarenes, a supramolecular 1D structure is formed by the combination of the H-bonded synthon and the π -stacking of the phenyl rings, as, for example, in the associate of 18-crown-6 with 2,4-dinitrophenylhydrazine [22]. This specified type of a non-covalent interaction takes place when the ratio arene:crown is 2:1. In our practice of designing associates of polyfluoroaromatic diamines, the formation of that kind of an associate was registered upon the co-crystallization of hexafluoro-2,7-naphthylenediamine and 18-crown-6 [11]. The development of this research using various polyhalogenated arylenediamines is of a fundamental interest.

The purposes of the present work are (i) to test the possibility of obtaining co-crystals of polyfluorinated *meta*-arylenediamines and 18-crown-6 of stoichiometry 2:1, (ii) to study in detail their supramolecular architecture, and (iii) to elucidate the structural features of the components affecting the self-assembly pattern. Polyfluoro (het)arylenediamines with various substituents (Fig. 2), forming the 1:1 associates [11–14], were used as the test objects.

2. Experimental

2.1. Measurements

1H and ^{19}F NMR spectra were recorded on a Bruker AV-300 spectrometer using residual protons of the deuterated solvent and C_6F_6 ($\delta = -163$ ppm from CCl_3F) as internal standards; δ are given in ppm relative to TMS and CCl_3F , J are given in Hz. IR spectra were recorded on a Bruker Vector-22 spectrometer for KBr pellets. Melting points were determined on an Apotec RS instrument.

Single crystal X-ray diffraction study of associates and individual polyfluoroarenes was performed on a Bruker Kappa Apex II diffractometer equipped with a two-dimensional CCD-detector using ω , φ scanning. Absorption correction was applied using the SADABS program. The structures were solved by the direct method and refined by full-matrix least-squares method in an anisotropic approximation (except H atoms) using the SHELXL-97 program [23]. Positions of hydrogen atoms of amino groups were found from difference map and refined isotropically, the rest hydrogen atoms were located geometrically and refined in the riding model. CF_3 group in the co-crystal **2H-cr** is disordered in the ratio 0.906(8):0.094(8). The intermolecular interactions were analyzed using PLATON [24] and MERCURY programs [25].

Thermal analysis was performed with a differential scanning calorimeter NETZSCH DSC 204 F1 Phoenix. DSC measurements were carried out by heat flow measurement method at a constant heating rate of 9 K min^{-1} in 25 mL min^{-1} Ar flux. Powdered samples of precipitates or single crystals with a mass 3–12 mg were distributed uniformly over the bottom, carefully tamped and cold sealed in aluminum crucibles. The baseline signal obtained by heating two empty crucibles was subtracted from the experimental results of samples. Netzsch Proteus Analysis software was used to determine DSC peak areas and transition temperatures values. The transition temperatures were defined from the resulting heat flow as intersections of the peak onset with the corresponding baseline. The peak area determination was performed by integrating the area between the measurement curve and the integral tangential baseline. The sensitivity of the sample carrier sensors and temperature scale graduation were calibrated by melting and crystal-to-crystal transition measurements of standard samples (cyclohexane, adamantane, Hg, Ga, naphthalene, benzoic acid, KNO_3 , In, Sn) [26].

S3 MICRO (HECUS) small angle diffractometer (Cu $K\alpha$, 50 W) with a point collimation of primary beam was used for measuring scattering patterns of samples. The scattering vector magnitude $h = 4\pi \sin(\theta)/\lambda$ (where 2θ is the scattering angle, and $\lambda = 1.541\text{ \AA}$ is the radiation wavelength) was used as the scattering coordinate. The scattering intensity was measured within the range of the scattering vector magnitudes $0.01 < h < 0.6\text{ \AA}^{-1}$. All measurements were performed with *n*-hexane solutions of samples in quartz capillaries. SAXS patterns of pure solvents were subtracted from the corresponding SAXS patterns of the solutions with taking into account the X-ray absorption coefficients. ATSAS software was used for the data treatment [27]. The radius of gyration of the particles (R_G) was determined by the slope of the small angle curve in coordinates ($\ln(I(h)); h^2$), and the radius of gyration of the cross section of the particles ($R_{G(\text{cross})}$) was determined by the slope of the small angle curve in coordinates ($\ln(I(h)*h); h^2$) to compare the

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