Supramolecular 1D assemblies of polyfluorinated arylenediamines and 18-crown-6

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Rods (1D assemblies) formed by alternate crown ether and arylenediamine molecules are the motif of the supramolecular architecture of crystals of molecular associates of 18-crown-6 with tetrafluoro-1,4- and -1,3-phenylenediamines, hexafluoro-2,6- and -2,7-naphthylenediamines. Molecules in the assemblies are arranged *via* H-bond predominantly between the crown ether oxygen atoms and the polyfluoroarene amino group hydrogen atoms. Influence of the amino groups mutual arrangement and the aromatic framework size on the crystal supramolecular architecture is characterized. Specific melting heats of the crystalline 1D assemblies of *para*- and pseudo-*para*-arylenediamines are higher than those of *meta*- and pseudo-*meta*-analogs; the associates having higher melting heats selectively crystallize from solutions of isomeric phenylene- or naphthylenediamine mixtures.

Key words: molecular crystals, supramolecular architecture, X-ray diffraction analysis, polyfluorinated compounds, arylenediamines, crown ether, melting heat, high-performance materials.

Crown ethers, in particular, 18-crown-6, and compounds containing an amino group form molecular crystals, which is confirmed by reproducible stoichiometry of the components and melting points differing from characteristics of the individual compounds.[1] The Cambridge Structural Database[2] contains information on structures of 70 associates of 18-crown-6 with different amines. In them, the amino group is bonded by the hydrogen bond with one or two oxygen atoms of the crown ether.[3] And in the crystals, there are represented the amine—crown or amine—crown—amine groups isolated in space (the stoichiometry of the components is 1 : 1 and 1 : 2, respectively). In the latter case, two molecules of the amino compound flank the plane of the crown ether.[4] The presence of two amino groups in one molecule gives an opportunity to form polymolecular associates, *i.e.*, one-dimensional supramolecular 1D assemblies, which motif is the rod (chain, line) from alternating units ...—crown—diamine—... Among the known associates involving 18-crown-6, examples of 1D assemblies based exclusively on the supramolecular synthon[5] C_{crown}—O...H—N are not numerous: these are associates of bis-thiourea ($H_2NC(S)NHNHC(S)NH_2$) and dithiooxamide ($H_2NC(S)C(S)NH_2$).[6] Most of the 1D assemblies are formed at least by two different synthons. For example, in the associate of 18-crown-6 with thiourea[7] of stoichiometry 1 : 2, the synthon C=S...H—N formed by two thiourea molecules is also involved into the construction of the elemental unit of the rod. The authors in work[8] consider the fragment C_{crown}—O...H—CH_2—N as the second synthon forming the rod in the methylthiourea associate, *i.e.*, they suggest involvement of the "acidic" hydrogen of the methyl group into the formation of a hydrogen bond. In the associate of 18-crown-6 with 2,4-dinitrophenylhydrazine[9] of stoichiometry 1 : 2, the synthon C_{crown}—O...H—N is combined with the π-stacking interaction of the phenyl rings. Considerable amount of associates of 18-crown-6 and amines are two- and three-dimensional constructions.

From the point of view of crystal engineering, supramolecular architecture based on 1D assemblies is promising since it suggests anisotropy of physical properties of the crystals, which is the higher the less is the interaction of the 1D assemblies between each other. This circumstance can be used in the development of high-tech functional materials and suggests the urgency of design of organic crystals based on 1D assemblies, first of all those, which,

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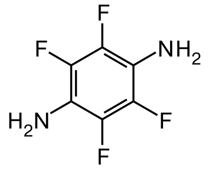
due to the specificity of the chemical structure of molecule-components, possess additional possibilities for transmission of effects along the rod. Such a possibility is provided, for example, by the conjugation chain involving the aromatic ring and synthons forming the rod, due to which it is able to transmit a signal (for example, disturbance of electron density) to the other end of the supramolecular assembly with insignificant loss of its intensity.

Earlier,[10,11] we have reported on the formation of two-component crystalline associates of 18-crown-6 and polyfluorinated *para*- and *meta*-phenylenediamines or pseudo-*para*- and pseudo-*meta*-naphthylenediamines from solutions in *tert*-butyl methyl ether. When amount of the crown ether is insufficient, crystallization of the mixture of isomeric arylenediamines occurs selectively with respect to *para*- and pseudo-*para*-isomers. The effect of "molecular recognition" found empirically was used during preparation of polyfluoroarylenediamines in the highly pure state with subsequent use in the synthesis of polyimides,[12] analogs of known material for optical applications[13]. In addition, these pairs of compounds *a priori* meet requirements for the construction of crystalline 1D assemblies.

The purpose of the present work consists in the revealing specificities of supramolecular architecture of crystals of two-component associates of 18-crown-6 and polyfluorinated arylenediamines, as well as possible reasons of isomeric selectivity during formation of crystal phase.

In this work, we used tetrafluoro-1,4- and -1,3-phenylenediamines, hexafluoro-2,6- and -2,7-naphthylenediamines (*para*-, *meta*-, pseudo-*para*-, and pseudo-*meta*-isomers **1**—**4**, respectively) and 18-crown-6. Such a set of aromatic substrates allows us to characterize the influence of the aromatic framework size and mutual arrangement of the amino groups on the supramolecular architecture and properties of the crystalline associates.



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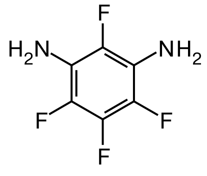

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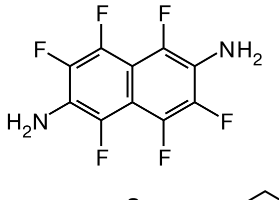

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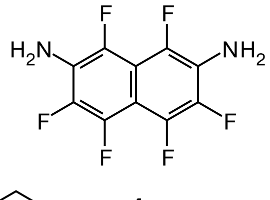

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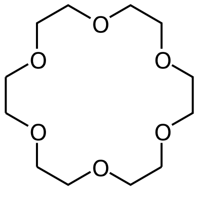

18-Crown-6

Results and Discussion

X-ray diffraction analysis of associates. Crystal associates of 18-crown-6 and tetrafluoro-*para*-phenylenediamine ($C_{12}H_{24}O_6 \cdot C_6H_4N_2F_4$ (**K-1**)), tetrafluoro-*meta*-phenylenediamine ($C_{12}H_{24}O_6 \cdot C_6H_4N_2F_4$ (**K-2**)), hexafluoropseudo-*para*-naphthylenediamine ($C_{12}H_{24}O_6 \cdot C_{10}H_4N_2F_6$ (**K-3**)) and hexafluoropseudo-*meta*-naphthylenediamine ($C_{12}H_{24}O_6 \cdot 2C_{10}H_4N_2F_6$ (**K-4**)) are formed upon mixing solutions of equimolar amounts of the components in low-polar aprotic solvents. Associates **K-1**—**K-3** have stoichiometry of 1 : 1, in associate **K-4**, the proportion 18-crown-6 : **4** is 1 : 2. The crystallographic data and parameters of the structure refinements are given in Table 1.

Single-crystal X-ray diffraction analysis of the structure of compound **1** was reported in Ref. 14, the data on the structures of compounds **2**—**4** are absent. The bond distances C_{arom}—C_{arom}, C_{arom}—F and C_{arom}—N in the free diamine **1** and that included into associate **K-1** are approximately the same. Therefore, it can be suggested that the inclusion of molecules of polyfluoroarylenediamines **2**—**4** into the molecular associates with the crown ether will not considerably affect the interatomic distances in the molecules. In the naphthylenediamines **3** and **4** associated with 18-crown-6, there is realized the alternation of the bond distances C_{arom}—C_{arom} of the naphthalene framework (see, for example, Ref. 15). Note that in all the arylenediamines under consideration in the associates **K-1**—**K-4** and in the free diamine **1**,[14] the amino groups have a pyramidal structure, as well as in the crystalline adduct of 3,5-dinitro-1-cyanobenzene and 1,3-phenylenediamine.[16] The amino groups in associate **K-3** have the most planar structure. This is also indicated by the calculations by the DFT PBE/3Z method for compounds **1**—**4** (in the gas phase).

Supramolecular architecture of associates **K-1**—**K-4** has a general motif, the rods from the alternating molecules of arylenediamine and crown ether (Figs 1—4), the geometric characteristics of which are given in Table 2. The mutual coordination of the molecules in the rods is predominantly determined by the synthon C_{crown}—O...H—N (the geometrical parameters are given in Table 3). The contact C_{arom}—F...H—C_{aliph} with the distances less than the sum of the Van der Waals radii is found only in the rods of associates **K-1** and **K-4** (see Table 3).

The units and rods in the crystals of associates of *para*-phenylenediamine **K-1** and pseudo-*para*-naphthylenediamine **K-3** have virtually identical spatial structure (*cf.* Figs 1 and 3). The molecules of diamine and 18-crown-6 in associate **K-1** are arranged in special positions with the symmetry C_{2h}, whereas in associate **K-3**, with the sym-

Table 1. Crystallographic data and parameters of refinement of the structure of associates **K-1**—**K-4**

Parameter	**K-1**	**K-2**	**K-3**	**K-4**
Chemical formula	$C_{18}H_{28}F_4N_2O_6$	$C_{18}H_{28}F_4N_2O_6$	$C_{22}H_{28}F_6N_2O_6$	$C_{32}H_{32}F_{12}N_4O_6$
Molecular weight	444.42	444.42	530.46	796.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/m$	$P2_1/n$	$C2/c$	$P\bar{1}$
a/Å	8.243(4)	7.565(7)	20.617(2)	9.322(1)
b/Å	16.916(8)	16.10(1)	9.845(1)	9.330(1)
c/Å	8.857(4)	18.31(2)	15.854(2)	11.037(1)
α/deg	90	90	90	95.191(7)
β/deg	115.997(7)	100.33(2)	129.840(6)	108.697(8)
γ/deg	90	90	90	107.583(8)
V/Å^3	1110.1(9)	2194(3)	2470.9(5)	848.0(2)
Z	2	4	4	1
d_{calc}/g cm^{-3}	1.330	1.346	1.426	1.560
μ/cm^{-1}	1.20	1.21	1.32	1.51
Number of measured/independent reflections	4298/833	16362/3192	2494/2425	3512/3297
Number of reflections with $I > 2\sigma(I)$	742	1996	1334	1962
Number of refining parameters	102	271	188	273
R_1 for $I > 2\sigma(I)$	0.0432	0.0916	0.0919	0.0613
wR_2 for all the reflections	0.1038	0.2236	0.3109	0.2200
GOOF	1.125	1.089	1.114	1.028

metry C_i. The conformation of the crown ether in associate **K-1** is close to the classic crown D_{3d}: 3(TGT,TǦT).[17] There is a disorder of positions of some atoms of 18-crown-6 in associate **K-3**, but the conformation of the main part of the molecule is also close to D_{3d}: 3(TGT,TǦT). The centers of masses of the molecules of the rods **K-1** and **K-3** components are on the rod axis, the slopes of the planes of 18-crown-6 and arylenediamines to the axis are different (see Table 2; Fig. 5, *a*). It cannot be excluded that the angle formed by the planes of the crown ether and arylenediamine molecules is affected by the degree of pyramidality of the amino groups and is optimum from the point of view of the hydrogen bonding efficiency. The arylenediamine molecules do not virtually go beyond the perimeter of the rod cross-section (see Figs 1, *c* and 3, *c*). The length of the elemental unit in the assemblies (see Table 2) is determined by the size of the aromatic framework of the diamine: the distance between molecules of the crown ether in the rod increases from **K-1** to **K-3**.

The structure of the 1D assembly of associate **K-2** is given in Fig. 2. The molecule of 18-crown-6 is in the conformation C_i: 2(TGT,TGT,GGT)[17] and is placed in the center of symmetry, whereas the molecule of diamine **2** is in general position. The mutual arrangement of the components in the rod considerably differs from that in **K-1** and **K-3**: the planes of the neighboring crown ether molecules in **K-2** are arranged the zigzag (see Figs 2, *b* and 5, *b* and Table 2). The plane of the molecule of phenylenediamine **2** is parallel to the rod axis, the center of its mass is shifted to the periphery, approximately half of the molecule goes beyond the perimeter of the rod cross-section (see Fig. 2, *c*), but the amino groups are arranged close enough to its axis. The length of the rod elemental unit in **K-2** is less than in **K-1**. It is obvious that such a structure of 1D assembly is due to the mutual *meta*-arrangement of the amino groups in phenylenediamine **2**.

Associate **K-4** differs in the stoichiometry of the components from those considered above (see Fig. 4, *a*), however, a supramolecular 1D-motif with the in-pairs parallel arrangement of the components similar to that in associ-

Table 2. Supramolecular parameters of rods of associates **K-1**—**K-4**

Parameter	**K-1**	**K-2**	**K-3**	**K-4**
Direction of the rod axis	$a + c$	b	$a + b$, $a - b$	$a + b + c$
Length of the rod unit/Å	9.08	8.05	11.4	12.6
Slope of the plane of 18-crown-6 to the rod axis/deg	77	37, 143	71	82
Slope of the plane of diamine to the rod axis/deg	20	0	77	21
Angle between the 18-crown-6 planes/deg	0	107	0	0

ates **K-1** and **K-3** is present in the structure of its crystals as well (see Figs 4, *b* and 5, *c*). Two molecules of diamine **4** bound by the π-stacking interaction are present between the molecules of crown ether in the rod: the centers of masses of the molecules are displaced from the rod axis to the periphery, the planes of the molecules are arranged by the type «face-to-face» with the shift (the interplane and intercentroid distances are 3.33 and 3.59 Å, respectively) and turn by 180°. Such distances are characteristic of the π-stacking, in which the pairs arene—polyfluoroarene are involved (the stabilization energy is ~18—29 kJ mol^{-1})[18] or, considerably more seldom, polyfluoroarene—polyfluoroarene (the stabilization energy ~16—23 kJ mol^{-1}).[19]

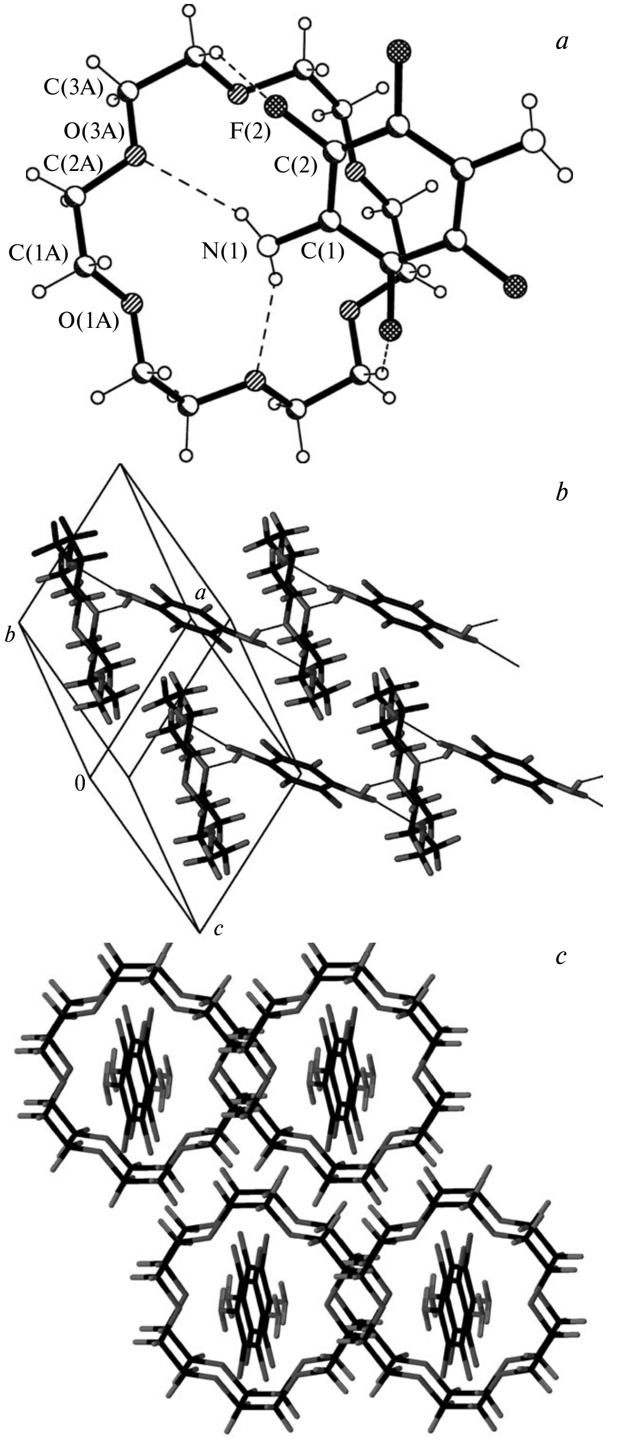

Fig. 1. Structure of associate **K-1**: the fragment of the rod (here and in Figs 2—4 the numeration is given for atoms in the independent part of the unit cell) (*a*); plane of the rods, the view from above (*b*); planes of the rods, the view along the rod axis (*c*).

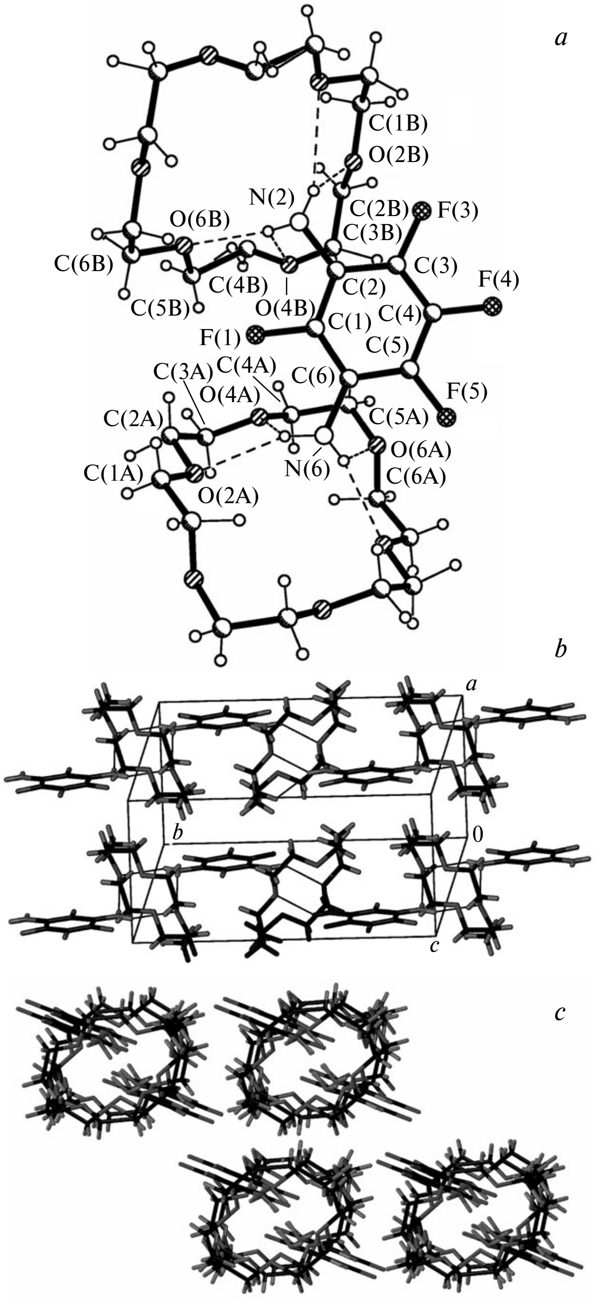

Fig. 2. Structure of associate **K-2**: fragment of the rod (*a*); plane of the rods, the view from above (*b*); planes of the rods, the view along the rod axis (*c*).

It cannot be excluded that the π-stacking in a certain degree is due to the dipole-dipole interaction[18,20] of two molecules of diamine **4**. Static polarization of the electron density, when the amino groups in the naphthalene framework have the pseudo-*meta*-arrangement, develops a dipole along the bond C(9)—C(10); different directions of the dipoles in the molecules turned by 180° provides their mutual π-coordination. Two amino groups from different molecules of the diamine, imitating pseudo-*para*-arranged substituents, are involved into the formation of the hydrogen bonds with molecules of 18-crown-6 (see Fig. 5, *c*). This is the reason that the supramolecular structure of 1D assembly **K-4** based on the pseudo-*meta*-naphthylenediamine is similar to the structure of associates **K-1** and **K-3** based on the *para*- and pseudo-*para*-arylenediamines (the in-pairs parallel arrangement of the molecules), rather than to the structure of associate **K-2** based on the *meta*-phenylenediamine (the zigzag arrangement of the molecules). The configuration of the "dimer" formed by the molecules of diamine **4** and its slope to the rod axis are so that the length of the elemental unit of the rod **K-4** is somewhat larger than the length of the unit of the rod **K-3**.

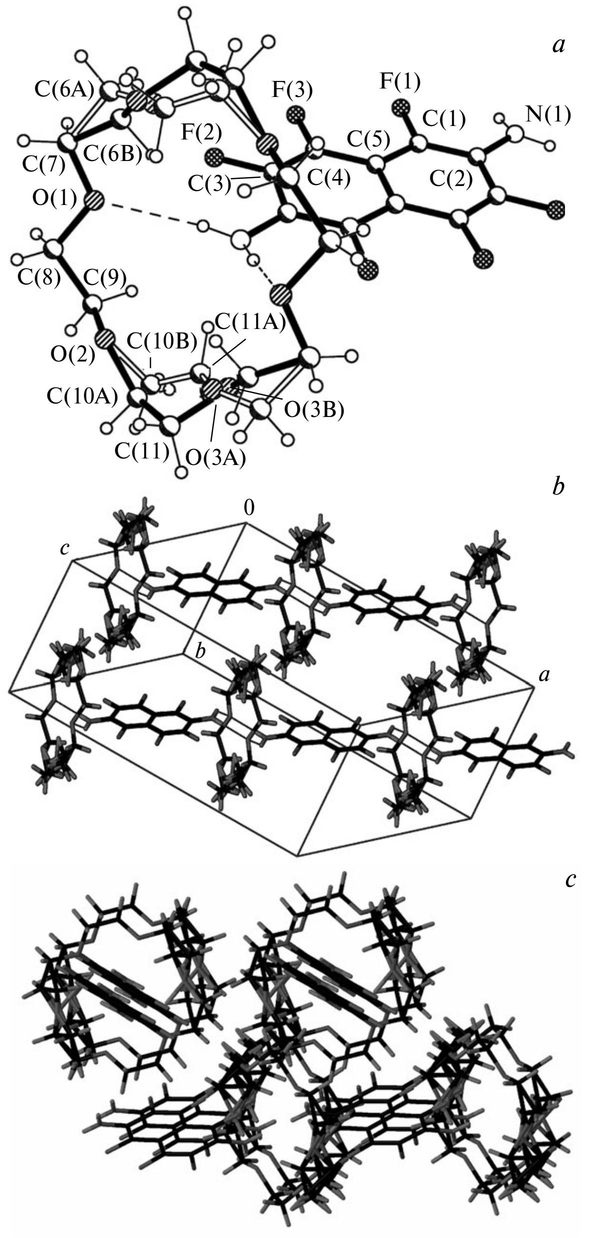

Fig. 3. Structure of associate **K-3**: fragment of the rod (*a*); plane of the rods, the view from above (*b*); planes of the rods, the view along the rod axis (*c*).

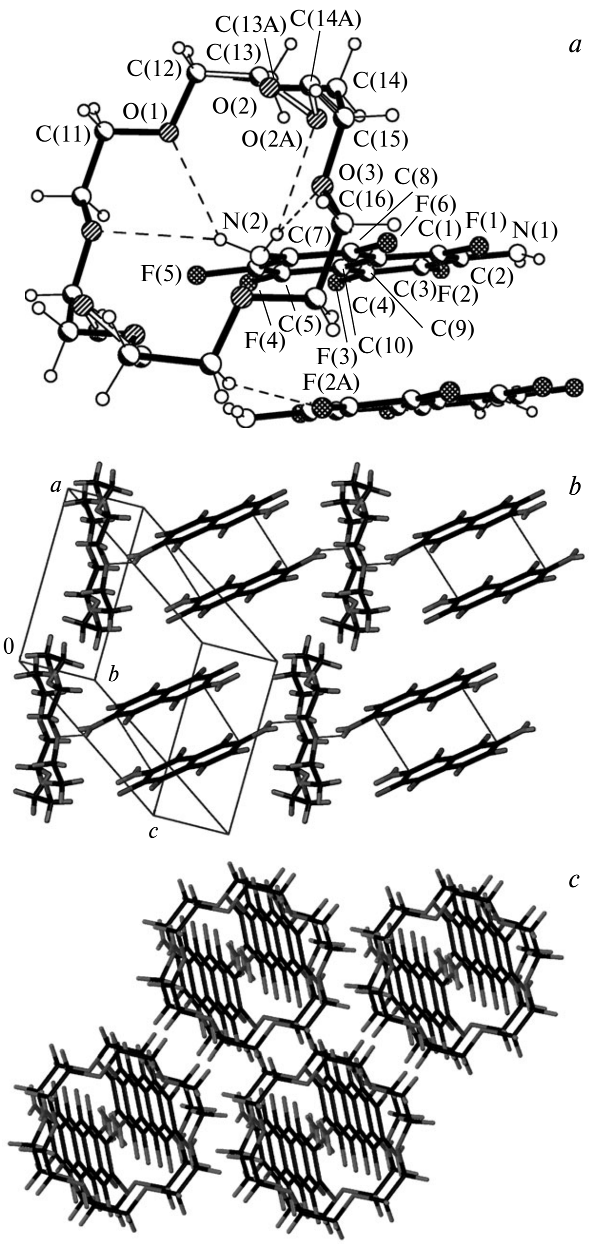

Fig. 4. Structure of associate **K-4**: fragment of the rod (*a*); plane of the rods, the view from above (*b*); planes of the rods, the view along the rod axis (*c*).

Table 3. Parameters of interactions $\mathrm{C_{crown}}$—O...H—N and $\mathrm{C_{arom}}$—F...H—$\mathrm{C_{aliph}}$ in the rods of associates **K-1**—**K-4**

Associate	Interaction	$l_{\mathrm{X...Y}}$	$l_{\mathrm{H...Y}}$	Angle X—H...Y/deg
		Å		
K-1	N(1)—H(11)...O(3A)	3.242(3)	2.45(2)	160(2)
	C(3A)—H(3AB)...F(2)	3.354(4)	2.44(3)	152(2)
K-2	N(2)—H(2B)...O(6B)	3.182(6)	2.45	144
	N(2)—H(2A)...O(6B)	3.353(7)	2.55	156
	N(6)—H(6A)...O(2A)	3.213(6)	2.40	157
	N(6)—H(6B)...O(2A)	3.162(6)	2.42	145
K-3	N(1)—H(1B)...O(1)	3.14(1)	2.31(7)	163(5)
	N(1)—H(1A)...O(1)	3.408(8)	2.57(5)	170(6)
K-4	N(2)—H(2A)...O(3)	3.211(5)	2.36(5)	171(5)
	N(2)—H(2B)...O(3)	3.559(6)	2.69(4)	161
	C(16)—H(16A)...F(5)	3.272(5)	2.49	138
	C(12)—H(12A)...F(2)	3.386(6)	2.50	151
	C(11)—H(11B)...F(2)	3.42	2.57	146

The rods of associates **K-1**—**K-3** are based on the synthon of the same type, *i.e.*, $\mathrm{C_{crown}}$—O...H—N. The π-stacking interaction of two molecules of naphthylenediamines are additionally involved into the formation of the rod **K-4**. Shortened contacts between the atoms of the neighboring rods in the crystals of associates **K-1**—**K-3** are absent. In the crystal **K-4**, there is present a shortened contact between the hydrogen atom of the amino group, which is not involved into the formation of the rod, and the fluorine atom of the molecule of arylenediamine from the neighboring rod (N(1)—H(1A)...F(4)-$\mathrm{C_{arom}}$), which is not comparable in its strength[21] with the interactions supporting the structure of the rod. To sum up, the supramolecular architecture of associates **K-1**—**K-4** have the motif not higher than 1D supplemented by a weak inter-rod interaction in associate **K-4**.

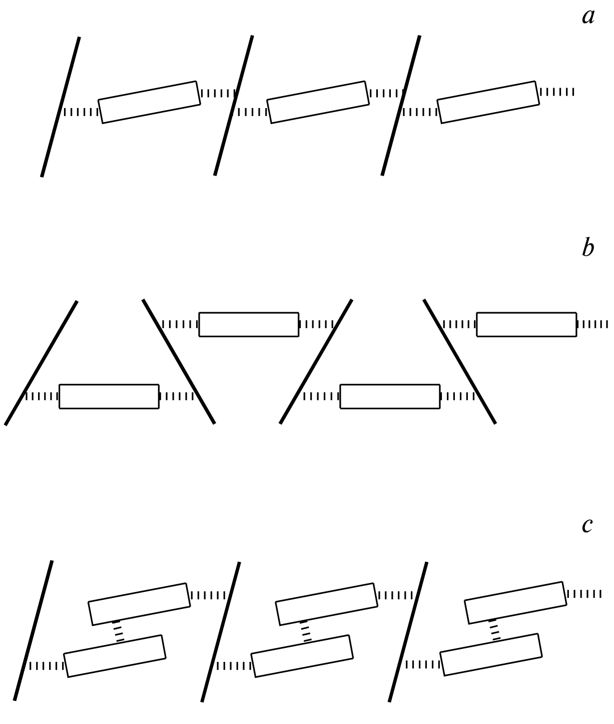

Fig. 5. Graphical picturing of the supramolecular 1D-motifs: associates **K-1** and **K-3** (*a*); **K-3** (*b*) and **K-4** (*c*).

Mutual arrangement of the 1D assemblies in crystals is different. In the crystals **K-3**, alternating layers of the parallel rods are clearly observed; rods are placed in the neighboring layers in the directions *a* + *b* and *a* – *b* at an angle 51° (see Fig. 3, *c* and Tables 2 and 4). Units in the neighboring rods are displaced with respect to each other both inside the layer and between the layers and are arranged by the type "ledge-to-cavity" (ledge is the crown ether molecule). This decreases the distance between the rod axes, which, as a result, becomes smaller than the rod diameter. In associates **K-1**, **K-2**, and **K-4**, the rods have a parallel placement in all the volume of crystals. Mutual displacement of the units in the neighboring rods of associates **K-1** and **K-4** reaches half of the unit length. In associate **K-2**, the molecules of *meta*-phenylenediamine play the part of ledges (see Fig. 2, *c*), the zigzag placement of the rods in crystal **K-2** is realized without displacement of the units with respect to each other.

In accordance with principle of close packing,[22] a criterion of layers in crystals **K-1**, **K-2**, and **K-4** is the maximum density of the supramolecular elements in the plane and/or the maximum rarefaction between the elements belonging to the neighboring layers. Using this criterion, it is possible to separate layers in **K-1** — plane a + c, a – c, in **K-2** — plane b, a, in **K-4** — plane a + b + c, a – b + c (see Table 4). This is the plane in **K-4**, in which the inter-rod contact is realized. It should be noted, however, that in associate **K-3**, in which arrangement of layers is obvious and defined by other criterion, *i.e.*, by parallelity of the rods (see above), the distance between the rods in the layer is larger than the distance between the rods in the neighboring layers (6.49 Å).

Table 4. Supramolecular parameters of the planes formed by the rods in the crystals of associates **K-1**—**K-4**

Parameter	K-1	K-2	K-3	K-4
Directions of the planes	a + c, a – c	b, a	a + b, a – b	a + b + c, a – b + c
Distances between the rod axes/Å	7.22	7.56	8.83	8.38
Shift of the rods with respect to each other/Å	3.96	~0	4.24	4.09
Angles between rods in the neighboring planes/deg	0	0	51.3	0

Thermal analysis of associates K-1—K-4. The study of thermal characteristics of associates **K-1**—**K-4** was performed in order to find a dependence between the melting (decomposition) heats of crystals and the supramolecular architecture and possible reasons of the isomeric selectivity during crystallization from solutions. Method of differential scanning calorimetry (DSC) was used to determine characteristic temperatures of the phase transition crystal-to-liquid and the value ΔH_W (specific melting weight heat), which is used to calculate the value ΔH_L (melting heat per unit) (Table 5). It was established that the value ΔH_W and melting points of crystals are reproducible in cyclic heating—cooling regime.

The value ΔH_W for associate **K-1** is higher than for associate **K-2** (*para*- and *meta*-phenylenediamines, respectively), whereas for associate **K-3** it is higher than for associate **K-4** (pseudo-*para*- and pseudo-*meta*-naphthylenediamines, respectively). Comparison of these results with the data on the selectivity of formation of crystals of associates from solutions of arylenediamine mixtures if shortage of the crown ether is present (associate **K-1** predominantly crystallizes from the mixture **1** + **2**,[10] whereas associate **K-3** from the mixture **3** + **4** (see Ref. 11)) indicates that crystallization from the solution takes place selectively in favor of the structure with higher heat of decomposition of the crystal lattice. Consequently, for the low-polar solvents the difference in contribution of isomers desolvation to the values of crystal formation heat can be neglected and the value ΔH_W can be considered as a measure of selectivity of crystallization of isomeric diamine associates.

On comparison of melting heats values for all the set of associates **K-1**—**K-4**, it is correct to operate with the values ΔH_L (see Table 5). Analysis of the ΔH_L dependence on the supramolecular architecture of 1D assemblies shows that the decrease of this value from **K-1** to **K-2** is apparently due to the change in the mutual arrangement of the molecules in the rod from the in-pairs parallel to the zigzag; whereas in the case of rods of the same structure going from **K-1** to **K-3**, due to the increase in the linear sizes of the units. Associates **K-3** and **K-4**, characterized by the in-pairs parallel structure of the rod and comparable linear sizes of the unit, have close values of ΔH_L. However, in this case it is necessary to take into account the different stoichiometry of the unit of associate **K-4**, as well as additional involvement of the synthon of another type (π-stacking) and half as large than in **K-1**—**K-3** amount of hydrogen bonds per one molecule of diamine. For example, allowance for the difference in stoichiometry of the components can be made by calculation of the melting heat of associate **K-4** per one molecule of diamine (ΔH_L*) (see Table 5). The value of ΔH_L* of associate **K-4** is less than ΔH_L of associate **K-3**, which is symbatic to the selectivity of crystallization of these associates from solution when shortage of the crown ether is present.

Table 5. Melting points and melting heats of associates **K-1**—**K-4** according to the DSC

Associate	T_{onset}	T_{max}	ΔH_W /J g^{-1}	ΔH_L (ΔH_L*) /kJ mol^{-1}
	°C			
K-1	129.7	132.9	170	75.5
K-2	89.5	92.5	123	54.7
K-3	160.9	165.6	108	57.3
K-4	124.9	131.7	78	62.1 (41.4)

Note. T_{onset} is the temperature of the extrapolated onset of melting, T_{max} is the melting peak temperature, ΔH_W is the specific weighting melting heat, ΔH_L is the melting heat calculated on the weight of unit, ΔH_L* is the melting heat calculation on the weight of unit of **K-4** lacking one diamine molecule.

It should be note that the ratio of values ΔH_W found for the pairs of isomers (**K-1** *vs* **K-2** and **K-3** *vs* **K-4**) does not agree with the common concept on the influence of mutual arrangement of amino groups in the aromatic framework on the N—H bond polarization degree, as well as on the strength of the hydrogen bond formed by this fragment.[23] Obviously, the dependence of the crystals decomposition heat on this factor is mediated by the effects of the crystal lattice.

In conclusion, in this work we suggested a new group of objects for the crystals engineering — the associates of polyfluoroarylenediamines with 18-crown-6, which are supramolecular 1D assemblies based on the synthon C_{crown}—O...H—N; the π-stacking of two aromatic molecules is also involved into the formation of assembly **K-4**. We characterized the influence of mutual arrangement of the amino groups in the aromatic framework and its size on the architecture of crystals. In the associates of phenylenediamines going from *para*- (**K-1**) to *meta*-isomer (**K-2**), the in-pairs parallel arrangement of the molecules in the rod is changed to the zigzag one; contrary to this, in the associates of naphthylenediamines going from pseudo-*para*- (**K-3**) to pseudo-*meta*-isomer (**K-4**) the in-pairs parallel arrangement of the component planes in the rod remains the same due to the π-stacking of two molecules of arylenediamine and involvement of two amino groups from different molecules, imitating the pseudo-*para*-arranged substituents, into the formation of the rod. With increase of the linear sizes of the aromatic framework going from *para*- (**K-1**) to pseudo-*para*-arylenediamine (**K-3**), the structure of the rod is retained, but disparalleling of the rods in the neighboring layers occurs; in contrast to this, the stoichiometry and structure of the rod change going from *meta*- (**K-2**) to pseudo-*meta*-arylenediamine (**K-4**).

Experimental

^{1}H and ^{19}F NMR spectra were recorded on a Bruker AV-300 spectrometer, signals for the residual protons in the deuterated solvent and C_6F_6, respectively, were used as references. IR spectra were recorded on a Bruker Vector-22 spectrometer in the diffuse reflection mode. Thermal analysis was performed on a STA 409 PC Luxx Netzch synchronous thermal analyzer. Heating of the samples was performed under argon atmosphere at the rate 10 K min^{-1} to the temperature below the onset of the mass loss. Melting points for the samples were determined according to GOST 18995.4-73 on a Temp-2 apparatus in automatic mode. Quantum chemical calculations for the gas phase was performed by the PBE density functional method with the 3z basis using the PRIRODA program.[24]

Synthesis of crystalline associates of polyfluoroarylenediamines 1—4 with 18-crown-6 (general procedure). A solution of 18-crown-6 (2.8 g, 10.6 mmol) in *tert*-butyl methyl ether (10 mL) was added to a solution of polyfluorophenylenediamine (10 mmol, 1.7 g of diamines **1** and **2**, 2.7 g of diamines **3** and **4**) in *tert*-butyl methyl ether (10 mL) at room temperature with stirring. The mixture was kept for 1 h under these conditions. A precipitate formed was filtered off, washed with *tert*-butyl methyl ether, and dried. Monocrystals for X-ray diffraction were grown from the solutions of the associates in chloroform.

Associate of tetrafluoro-1,4-phenylenediamine (1) with 18-crown-6, 1 : 1 (K-1). The yield was 78%, m.p. 131—132 °C. ^1H NMR ($CDCl_3$), δ: 3.59 (br.s, 4 H, NH_2); 3.66 (br.s, 24 H, CH_2). ^{19}F NMR ($CDCl_3$), δ: 0.8 (s, F(2), F(3), F(5), F(6)). IR, ν/cm^{-1}: 3423, 3346, 3227 (NH_2); 2882, 2827, 1525, 1509 (C_{aliph}—H); 1624 (C_{arom}—C_{arom}); 1114 (C_{aliph}—O). Found (%): C, 48.75; H, 6.44; N, 6.28. $C_{18}H_{28}F_4N_2O_6$. Calculated (%): C, 48.63; H, 6.35; N, 6.30.

Associate of tetrafluoro-1,3-phenylenediamine (2) with 18-crown-6, 1 : 1 (K-2). The yield was 60%, m.p. 89.5—90.5 °C. ^1H NMR ($CDCl_3$), δ: 3.62 (br.s, 24 H, CH_2); 3.79 (br.s, 4 H, NH_2). ^{19}F NMR ($CDCl_3$), δ: −9.9 (m, 2 F, F(4), F(6)); −6.4 (m, 1 F, F(5)); 1.8 (m, 1 F, F(2)). IR, ν/cm^{-1}: 3435, 3415, 3390, 3384, 3262, 3177 (NH_2); 2892, 1514 (C_{aliph}—H); 1635 (C_{arom}—C_{arom}); 1109 (C_{aliph}—O). Found (%): C, 48.70; H, 6.48; N, 6.25. $C_{18}H_{28}F_4N_2O_6$. Calculated (%): C, 48.63; H, 6.35; N, 6.30.

Associate of hexafluoro-2,6-naphthylenediamine (3) with 18-crown-6, 1 : 1 (K-3). The yield was 75%, m.p. 161—162 °C. ^1H NMR (DMSO-d_6), δ: 3.50 (s, 24 H, CH_2); 5.74 (br.s, 4 H, NH_2). ^{19}F NMR (DMSO-d_6), δ: 8.1 (m, 2 F, F(4), F(8)); 10.3 (m, 2 F, F(3), F(7)); 15.6 (m, 2 F, F(1), F(5)). IR, ν/cm^{-1}: 3435, 3342, 3228 (NH_2); 2884, 1532, 1469 (C_{aliph}—H); 1616, 1661 (C_{arom}—C_{arom}); 1103 (C_{aliph}—O). Found (%): C, 49.89; H, 5.44; N, 5.26. $C_{22}H_{28}F_6N_2O_6$. Calculated (%): C, 49.79; H, 5.32; N, 5.28.

Associate of hexafluoro-2,7-naphthylenediamine (4) with 18-crown-6, 2 : 1 (K-4). The yield was 58%, m.p. 126—127 °C. ^1H NMR (DMSO-d_6), δ: 3.50 (s, 24 H, CH_2); 5.94 (br.s, 8 H, NH_2). ^{19}F NMR (DMSO-d_6), δ: 5.3 (m, 4 F, F(3), F(6)); 9.2 (m, 4 F, F(4), F(5)); 13.4 (m, 4 F, F(1), F(8)). IR, ν/cm^{-1}: 3485, 3440, 3385, 3347, 3231 (NH_2); 2887, 1486 (C_{aliph}—H); 1666, 1617 (C_{arom}—C_{arom}); 1111 (C_{aliph}—O). Found (%): C, 48.34; H, 4.11; N, 6.95. $C_{32}H_{32}F_{12}N_4O_6$. Calculated (%): C, 48.24; H, 4.02; N, 7.03.

X-ray diffraction study of associates K-1—K-4. X-ray diffraction experiment for associates **K-1** and **K-2** was performed on a SMART APEX diffractometer (Mo-Kα radiation, ϕ- and ω-scanning, $\theta < 23.5°$), for associates **K-3** and **K-4**, on a BRUKER P4 diffractometer (Mo-Kα radiation, θ/2θ-scanning, $\theta < 26°$) at room temperature. The crystallographic data and parameters of refinement of the structures are given in Table 1. The structures were solved by the direct method and refined in the anisotropic-isotropic approximation using the SHELXL-97 program.[25] Positions of the hydrogen atoms of 18-crown-6 in crystals **K-2**—**K-4** were specified geometrically and refined using the riding model. In crystal **K-3**, a disorder of a number of crown ether atoms in proportion 0.37 : 0.63 was observed, which was the reason to set geometrical limitations in the refinement. In crystal **K-4**, a number of crown ether atoms are disordered in proportion 0.23 : 0.77. The minor part of the disordered atoms in **K-3** and **K-4** was refined in isotropic approximation. Geometrical analysis was performed using the PLATON program.[26]

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