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X-RAY DIFFRACTION STUDY OF PERFLUORO-9,10-DIPHENYLANTHRACENE AND PERFLUORO-9,10-DIPHENYLDIHYDROANTHRACENES

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The molecular and crystal structure of perfluoro-9,10-diphenylanthracene and its perfluorinated dihydro derivatives (9,10-diphenyl-1,4-dihydroanthracene, 9,10-diphenyl-2,9-dihydroanthracene, and *cis*,*trans*-9,10-diphenyl-9,10-dihydroanthracenes) is determined by single crystal X-ray diffraction. 9,10-Diphenyl-2,9-dihydroanthracene is analyzed in cocrystal with 9,10-diphenyl-1,4-dihydroanthracene (2:1). It is shown that in the studied compounds the angles between the planes of the phenyl rings and the anthracene core are close to 90°. According to the DFT/B3LYP/6-31G(*d*) calculations, 9,10-diphenyl-1,4-dihydroanthracene is most thermodynamically stable among the studied dihydroanthracenes. There are C–F…π interactions and no π-stacking interactions in the crystals of the studied compounds.

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INTRODUCTION

A field of the practical application of perfluorinated polynuclear aromatic compounds is microelectronics: for example, perfluorinated pentacenes, oligofluorenes, oligo- and polyphenylenes are used as semiconductor materials in organic light-emitting diodes (OLEDs), field-effect transistors (OFETs), photocells, and so on [1-6]. 9,10-Diphenylanthracene (DPA) and its derivatives containing substituents in the anthracene core and phenyl substituents are also of interest for microelectronics, e.g., chemiluminescent luminophors [7, 8]. DPA holds a special place among the ever growing family of organic semiconductors [9] due to their high electron-hole mobility [10]. It is known that fluorine substitution for hydrogen atoms can substantially alter the properties of compounds and affect intra- and intermolecular interactions [11].

The Cambridge Structural Database (CSD) [12] contains information on the crystal structure of DPA and some of its derivatives. Perfluoro-9,10-diphenylanthracene (**1**) is an unknown compound. Accordingly, this work aims to study the molecular and crystal structure of compound **1** and isomeric perfluoro-9,10-diphenyldihydroanthracenes: 9,10-diphenyl-1,4-dihydroanthracene (**2**), 9,10-diphenyl-2,9-dihydroanthracene (**3**), *cis*-9,10-diphenyl-9,10-dihydroanthracene (**4**), and *trans*-9,10-diphenyl-9,10-dihydroanthracene (**5**).

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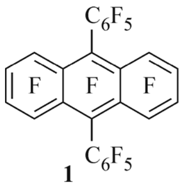
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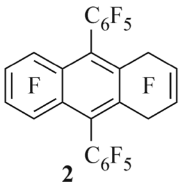
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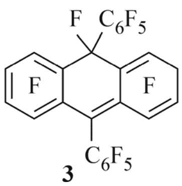
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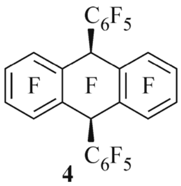
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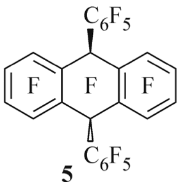
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EXPERIMENTAL

Compounds 1-5 were synthesized in the perfluorobenzocyclobutene reaction with an excess of pentafluorobenzene in the antimony pentafluoride medium [13]. **Compound 1.** $T_{\mathrm{melt}} = 220\text{-}221$ °C. **Compound 2.** $T_{\mathrm{melt}} = 232\text{-}237$ °C with decomposition, in a sealed capillary. **Compound 4.** $T_{\mathrm{melt}} = 267\text{-}268$ °C, in a sealed capillary. **Compound 5.** $T_{\mathrm{melt}} = 355\text{-}360$ °C with decomposition, in a sealed capillary. **Cocrystal 3**+**2** (2:1). $T_{\mathrm{melt}} = 174\text{-}180$ °C.

Single crystals of compounds 1-5 were prepared by slow evaporation of the solvent from the compound solutions: **1** (CH_2Cl_2–hexane), **2** ($CHCl_3$–hexane), **4** ($CHCl_3$), **5** (acetone). Cocrystals **3**+**2** (2:1) were prepared by slow evaporation from a solution of compounds **3**+**2** (3.3:1) in a $CHCl_3$–hexane mixture.

Single crystal X-ray diffraction. The single crystal X-ray diffraction analysis of compounds **1-5** was performed on a Bruker Kappa APEX II diffractometer (MoK_α radiation, graphite monochromator, CCD detector, φ, ω scanning, temperature 296 K). The absorption corrections were applied using the SADABS software. The structures were determined by a direct method using the SHELXS-97 software and refined by the least-squares technique in the anisotropic approximation using the SHELXL-97 software. The crystallographic data for compounds **1-5** and the refinement parameters are given in Table 1. The data have been deposited with CSD (CCDC 1547527-1547531) and are available free on request via the website www.ccdc.cam.ac.uk.

TABLE 1. Crystallographic Data and the Refinement Parameters for Compounds **1-5**

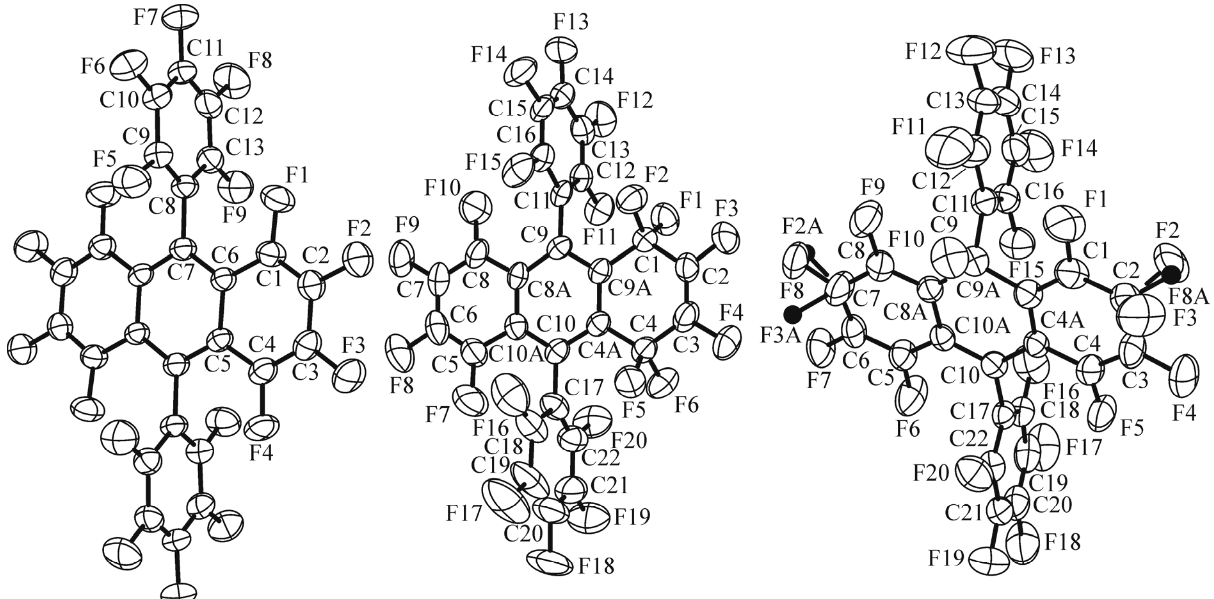
Parameter	**1**	**2**	**3+2**	**4**	**5**
Formula	$C_{26}F_{18}$	$C_{26}F_{20}$	$C_{26}F_{20}$ (2/3)**3**+(1/3)**2**	$C_{26}F_{20}$	$C_{26}F_{20}$
Molecular weight	654.25	692.26	692.26	692.26	692.26
Crystal symmetry	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group; *Z*	*P*2₁/*c*; 2	*Pbca*; 8	*P*-1; 3	*P*-1; 4	*P*-1; 1
a, Å	12.114(1)	21.538(2)	9.1800(5)	11.2632(4)	6.6445(3)
b, Å	8.419(1)	9.1318(8)	12.6381(7)	12.3686(4)	9.4975(4)
c, Å	12.301(2)	23.858(3)	15.9250(9)	17.0328(6)	9.5541(4)
α, deg			77.530(2)	87.506(2)	78.131(2)
β, deg	119.343(5)	90	79.633(2)	80.548(2)	89.942(2)
γ, deg			83.727(2)	80.607(2)	74.744(2)
V, Å^3	1093.6(2)	4692.5(8)	1769.8(2)	2308.9(1)	568.34(4)
d_{calc}, g/cm^3	1.987	1.960	1.949	1.991	2.023
μ, mm^{-1}	0.224	0.227	0.225	0.230	0.234
$\theta_{\max}$, deg	28.06	25.21	27.21	27.54	27.94
Completeness	0.992	0.991	0.988	0.997	0.994
I_{hkl} meas. /indep.	27925 / 2639	29468 / 4188	44126 / 7805	69530 / 10625	16573 / 2721
R_{int} / $I_{hkl} > 2\sigma(I)$	0.0258 / 2070	0.0696 / 2388	0.0295 / 5439	0.0350 / 7852	0.0240 / 2427
N_{par} / S	199 / 1.023	415 / 1.139	677 / 1.015	829 / 0.997	208 / 1.057
R_1 / wR_2 ($I > 2\sigma$)	0.0513/ 0.1377	0.0974/ 0.2933	0.0745 / 0.1477	0.0384/ 0.0986	0.0355/ 0.0986
R_1 / wR_2	0.0709/ 0.1866	0.1697/ 0.3728	0.1008 / 0.1646	0.0584/ 0.1224	0.0391/ 0.1027

The quantum chemical calculations were carried out with the GAMESS software [14] at the DFT level using the B3LYP functional and the standard 6-31G(*d*) basis set.

RESULTS AND DISCUSSION

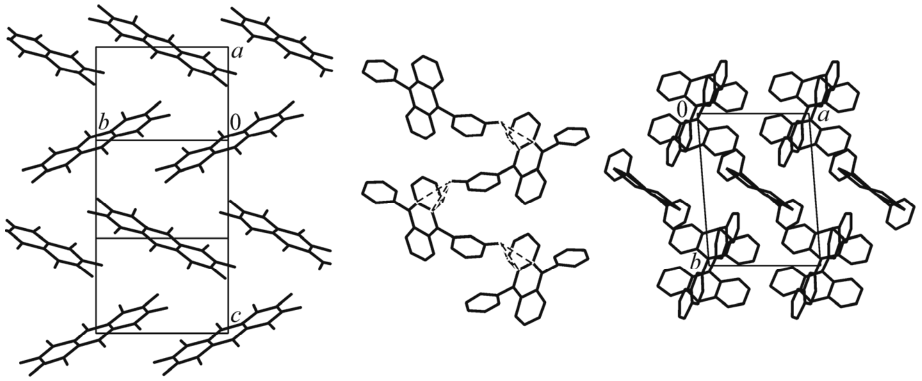
The structure of the centrosymmetric molecule in crystal **1** is shown in Fig. 1. The anthracene core of the **1** molecule is planar within ±0.020(3) Å. The bond lengths in it are close to the corresponding lengths in 1,2,3,4,5,6,7,8-octafluoro-9,10-diphenylanthracenee (OFDPA) [15]. The phenyl rings of the **1** molecule are turned out from the core plane and the interplanar angle between these planes is 88.1°. It is interesting to note that in the three known DPA polymorphs the corresponding interplanar angles are as follows: 67.0° in the most stable α form; 73.7°, 78.0° in the β form, and 90.0° in the least stable γ form [16]. In mentioned OFDPA diphenylanthracene this angle is 89.3° and in the 9,10-bis(pentafluorophenyl)anthracene molecule it is 68.3° [17]. Therefore, fluorination of the DPA molecular core leads to an increase in the turning angles of the phenyl rings. In the crystal molecular packing of **1** the *bc*-parallel layers with the herringbone packing of the anthracene moieties can be noted (Fig. 2), similar to the layers in the packing of the DPA α form. There are C–F…π (C1÷C6) interactions with the F2…centroid (Cg) distances of 3.281 Å and 3.831 Å in the layers. Note also the interlayer C–F…π(phenyl) interactions with the F4…Cg of 2.997 Å and F6…Cg distances of 3.555 Å and the shortened F9…C1 of 2.975 Å, F9…C2 contacts of 2.919 Å. The important role of C–F…π interactions in the supramolecular architecture of crystals was discussed in the review [18].

In the **2** molecule (Fig. 1) the anthracene moiety is also planar within ±0.080 Å, with a small (5.6°) bend of the tricyclic C1÷C9A system along the C1–C4 line. The angles between the planes of the phenyl rings C11÷C16, C17÷C22 and the anthracene core are 86.8° and 87.3° respectively. There are no similar structures in CSD, except only two 1,4-dihydroanthracene derivatives without a bridge between the C1 and C4 atoms [19] and with an almost planar core. In the **2** crystal the molecular ribbons along the *b* axis due to the C15–F14…π(C1–C9A) interactions with the F…Cg distance of 2.823 Å can be observed (Fig. 2). The molecular ribbons are bonded by C–F…π interactions with the F…Cg distances of 3.429 Å, 3.446 Å, and 3.583 Å. The most shortened intermolecular contacts are F3…F18 of 2.672 Å, F11…C2 of 2.968 Å.



1 **2** **3**

Fig. 1. Molecular structure of compounds **1-3** (thermal ellipsoids at the 50% probability level). The minor part in the disordered **3** molecule is shown by black balls.



1 **2** **3+2**

Fig. 2. Fragments of the molecular packing in the **1-3** crystals. For simplicity: the phenyl rings are not shown in **1**, only F14 is shown in **2**, and the fluorine atoms are not shown in **3**+**2**.

For compound **3** a cocrystal with dihydroanthracene **2** in a 2:1 ratio was obtained. There are two different molecules in crystal **3**+**2**: one is in a general position (**3** molecule), another is in a special position (**2** molecule), and both are disordered due to disordered fluorine atoms at the C2, C7, C23, and C26 atoms. If in the molecule in a special position (at the symmetry center) the fluorine atom sites are equally occupied (0.5:0.5), then in the molecule in a general position the fluorine atoms site are occupied in a ratio of 0.587:0.413(6). Therefore, the stoichiometry of cocrystal **3**+**2** is 2:1 and in total the unit cell of this crystal consists of three molecules. In the molecules of both **2** and **3** the anthracene core is planar within ±0.013 Å and ±0.095 Å respectively. In the **2** molecule the phenyl ring is turned by 88.5° from the core plane and in the **3** molecule the corresponding interplanar angles are 88.7° and 87.8° respectively for the phenyl rings C11÷C16 and C17÷C22. The arrangement of the C11–C16 ring in the **3** molecule allows us to say that there is the intramolecular C16–F15…π interaction with the central cycle of the anthracene core with the F…Cg distance of 2.633 Å. Since the molecules are disordered, the bond lengths cannot be analyzed. Note that CSD contains no information on the structure of 2,9-dihydroanthracene derivatives. The nearest analogue of compound **3** can be 1,2,2,3,4-pentafluoro-10-(2,3,4,5,6-pentafluorophenyl)-2,10-dihydrophenazine [20] where the interplanar angle between the pentafluorophenyl ring and the phenazine core is 86.2°. In the molecular packing of cocrystal **3**+**2** the *ac*-parallel layers of the **3** molecules alternating with the layers of the **2** molecules can be noted (Fig. 2). The molecules in the cocrystal are linked by a number of C–F…π interactions with the F…Cg distances of 3.093-3.959 Å.

Compounds **4** and **5** are the *cis* and *trans* isomers of perfluoro-9,10-diphenyl-9,10-dihydroanthracene (Fig. 3).

Two independent molecules in the **4** crystal have practically the same geometry. In both cases, the dihydroanthracene core is planar within ±0.126 Å and ±0.119 Å for two independent **4** molecules and within ±0.025 Å for **5**. A greater distortion of the core planarity in the **4** molecules is due to a small bend of 12.7° and 11.3° of the central cycle along the C9–C10 line. In the **4** and **5** molecules the angles between the planes of the phenyl rings and the anthracene core are close to 90°: 87.1°, 88.3°, 89.5°, 79.1° in **4** and 86.9° in **5**. Therefore, the conformation of the **4** and **5** molecules can be called crosswise, just as the conformation of the **1-3** molecules. CSD contains many data on the structure of 9,10-diphenyl-9,10-dihydroanthracene derivatives. Among the *cis* derivatives about half of the structures have the crosswise conformation. The other half of the structures is characterized by a conformation with a strongly bent anthracene core and the intramolecular π-stacking interaction between the phenyl rings. For example, in *cis*-9,10-bis(4-methoxyphenyl)-9,10-dihydroanthracene-9,10-diol [21] the bend angle of the dihydroanthracene cycle is 42.4° and the intercentroid distance is 3.634 Å. According to our DFT calculations, this conformation of the **4** molecule is 6.4 kcal/mol less favorable compared to the crosswise one observed in the crystal. For comparison, in the unfluorinated analogue the energy difference of these conformers is much smaller, being 1.5 kcal/mol. The *trans* derivatives have the crosswise conformation. An exception is the crystal of *trans*-9,10-

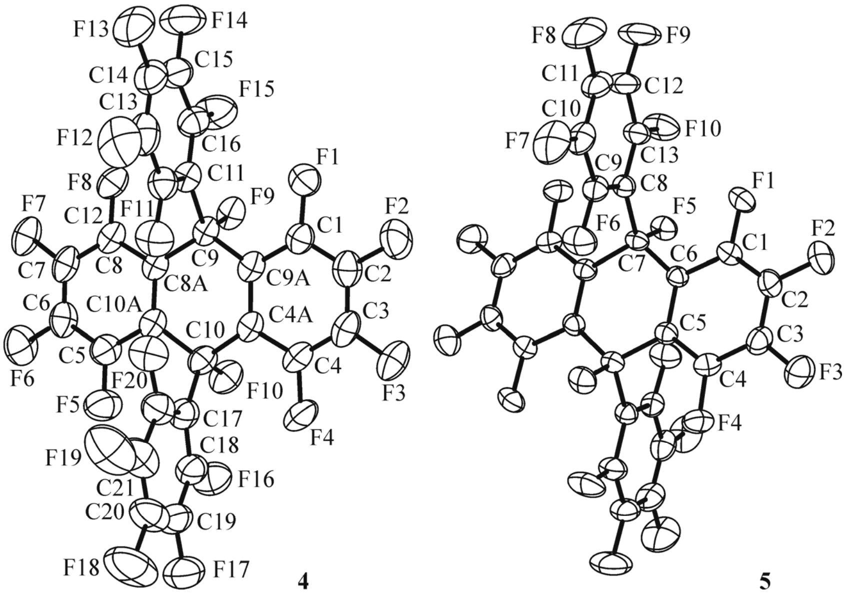


Fig. 3. Molecular structure of compounds **4** and **5** (thermal ellipsoids at the 50% probability level). For **4** one of two independent molecules is shown. The **5** molecule is located at the symmetry center.

dihydroxy-9,10-bis(4-*tert*-butylphenyl)-9,10-dihydroanthracene [22]. This crystal consists of two independent molecules, one of which has the crosswise conformation and another has a conformation with the anthracene core bent by 26.7° and one turned phenyl ring.

In the crystal molecular packing of compound **4** the C–F…π interactions between the fluorine atoms of the phenyl groups and the dihydroanthracene aromatic cycles are noteworthy. The shortest F…Cg distances are 2.958 Å, 3.056 Å, 3.086 Å. As a result of these interactions, the ribbons parallel to the *a* axis are formed. Via the additional F…F (2.709 Å, 2.795 Å) and F…C (3.044 Å) interactions the layers parallel to the *a*(*b*–*c*) plane are formed (Fig. 4). Among interlayer interactions note the F…F interactions with the distance of 2.717 Å. In the crystal of compound **5** the *bc*-parallel layers can also be observed (Fig. 4) formed via the C–F…π interactions of the F2, F7 atoms with the phenyl groups and the F8 atom with the aromatic cycles of the anthracene core with the F…Cg distances of 3.216 Å, 3.254 Å, 3.359 Å respectively.

Note the interlayer F5…C4 and F4…F6 interactions with the distances of 2.900 Å and 2.772 Å respectively.

Compounds **2-5** are isomeric 9,10-diphenyldihydroanthracenes. According to our DFT calculations, compound **2** containing the naphthalene moiety is most stable among them. The relative energies of isomers **2-5** are as follows:

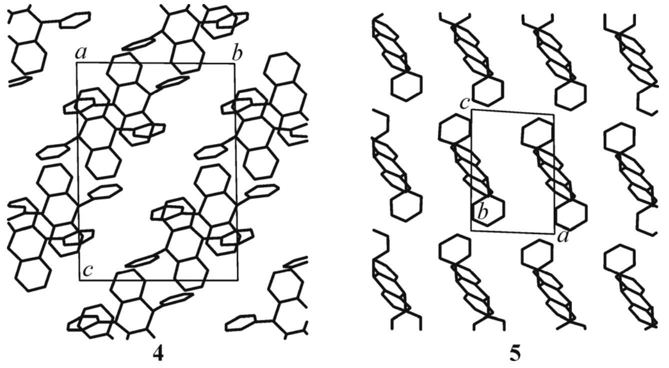


Fig. 4. Fragments of the molecular packing in the **4** (view along the *a* axis) and **5** (view along the *b* axis) crystals. For simplicity the F atoms are not shown.

0.0 kcal/mol (for **2**), 10.6 kcal/mol (for **5**), 14.0 kcal/mol (for **4**), and 22.1 kcal/mol (for **3**). From these calculations it follows that *trans* isomer **5** is 3.4 kcal/mol more stable than *cis* isomer **4**. For comparison, the energy difference of the analogous unfluorinated *trans* and *cis* isomers is only 0.2 kcal/mol.

CONCLUSIONS

The crystal and molecular structure of perfluorinated 9,10-diphenylanthracene and four isomeric 9,10-diphenyldihydroanthracenes is studied. Isomer **3** was investigated only as a cocrystal with isomer **2** (2:1). It is shown that in the studied compounds the angles between the planes of the phenyl rings and the anthracene core are close to 90°. According to the DFT/B3LYP/6-31G(*d*) calculations, isomer **2** containing the naphthalene moiety is the most stable among studied isomers **2-5**. In the **1-5** crystals there are C–F…π interactions and no π-stacking interactions.

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