INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are important persistent organic pollutants (POPs) of environment, which generally occur in all its parts: atmosphere, waters, soils, sediments and vegetation.1,2 The presence of PAHs in all these elements of the environment may establish a risk for humans as well as all living organisms. Migration and distribution of PAHs in the environment depends on their the physico-chemical properties, *i.a.* the water solubility, octanol-water distribution constant, or Henry's constants (volatility).3-5 Besides, in the gas-phase of atmosphere PAHs can react with nitrogen oxides, ozone, OH radicals and NO3 radicals, yielding *i.a.* nitrated, oxygenated, and hydroxylated derivatives of PAHs.6-9 The nitrated PAH compounds are potentially more mutagenic and carcinogenic than polycyclic aromatic hydrocarbon precursors.10

PAHs are released into the environment from domestic, industrial, and natural sources. Anthropogenic PAHs are usually generated from incomplete burning fossil fuels (*e.g.*, oil, coal, crude oil, gasoline)11,12, waste treatment11, combustion synthetic chemicals11, and other human activities, such as cooking, tobacco smoking, or vehicle traffic.13 The natural sources of emissions of PAHs pertain to: forest fires11, volcanic eruptions7, carbonization process, as products of humus conversion by microorganism14, diagenesis of organic matter15, *etc*.

Fluoranthene and acenaphthene are an example of the PAHs, which are classified as a priority control organic pollutants by the US Environmental Protection Agency (US EPA).16 Acenaphthene is also on the Hazardous Substance List. Fluoranthene and acenaphthene are considered non-carcinogens for humans, but should be handled with caution.17 Additionally, acenaphthene can be applied as intermediaries in pharmaceutical, agricultural, as well as chemical industries.17

EXPERIMENTAL

*Materials*

Fluoranthene (**I**) and acenaphthene (**II**) were provided by Sigma–Aldrich (Poland) at 98 % and at 99 % purity, respectively. The substances were investigated without further purification. Colourless crystals of **I,** suitable for X-ray analysis, were obtained by slow evaporation of ethanol-acetone mixture (1:1 v/v) at room temperature. On the other hand the crystals of acenaphthene were obtained upon recrystallization from petroleum ether, giving plate-shaped single crystals.

*X-Ray crystal structure determination*

The crystals of the **I** and **II** were mounted in turn on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo*K*α radiation (λ = 0.71073 ) at a room temperature, with *ω* scan mode. Ewald sphere reflections were collected up to 2*θ* = 50.10°. Lorentz, polarization and empirical absorption corrections using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm were applied.18 The structures were solved by the direct method and subsequently completed by difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares techniques. All hydrogen atoms were positioned in geometrically idealized positions and were allowed to ride on their parent atoms with Uiso(H) = 1.2 *Ueq*. The OLEX219 and SHELXS, SHELXL20 programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. All the graphics were prepared using ORTEP-321 for Windows, PLATON22, and MERCURY23.

*Physical measurements*

The infrared spectra of a polycrystalline samples (dispersed in KBr pellets) and monocrystalline samples of the fluoranthene and acenaphthene were recorded on a FT-IR Nicolet Magna 560 spectrometer by the transmission method with 2 cm-1 resolution at two temperatures, 293 and 77 K. The IR spectra were recorded in the spectral range of 4000-400 cm-1. Crystals of **I** and **II**, suitable for spectral studies, were obtained by crystallization from melted samples occurring between two closely spaced CaF2 windows. In this way thin enough crystals could be obtained, characterized by maximum absorbance at the νC-H band frequency range close to 0.5. Monocrystalline fragments were selected from the crystalline mosaic and spatially oriented, using a polarization microscope. In the next step, these selected crystals were exposed to the experiment by use of a metal plate diaphragm with a 1.5 mm diameter hole. The Raman experiment was performed using a WITec confocal CRM alpha 300 Raman microscope (Jagiellonian Centre for Experimental Therapeutics - JCET, Kraków). The spectrometer was equipped with an air cooled solid state laser operating at 532 nm and CCD detector which was cooled to -58 °C. The laser was coupled to the microscope via a single mode optical fiber with a diameter of 50 um. The scattered radiation was focused onto a multi-mode fiber (50 um diameter) and a monochromator. A dry Olympus MPLAN (50x/0.76NA) objective was used. The integration time for a single spectrum was 2 s. The spectra were collected in the range between 4000-120 cm-1 with the spectral resolution of 3 cm-1.

*Theoretical calculations*

The theoretical calculations were performed by means of the GAUSSIAN 0924 software package, using density functional theory (DFT) at the B3LYP level and with 6-31G(d, p) and 6-31G\*(d, p) basis sets for the acenaphthene, as well as 6-31+G(d, p) and 6-311++G(3df, 2pd) basis sets for the fluoranthene.25,26

The Hirshfeld surface analyses were carried out using the CrystalExplorer program.27 Distance from the Hirshfeld surface to the nearest nucleus inside and outside the surface has been marked by di and de, respectively. Whereas, dnorm is a normalized contact distance, which has been defined in turn of di, de and the van der Waals (vdW) radii of the atoms28:

  (1)

dnorm has been visualized using a red-white-blue colour scheme. If the atoms make intermolecular contacts closer than the sum of their vdW radii, these contacts will be represented as red spots on the surface. Longer contacts are blue, and white colour is used for contacts around the sum of van der Waals radii.28

RESULTS AND DISCUSSION

Molecular crystals of fluoranthene (**I**) and acenaphthene (**II**), as well as their derivatives have been the subject of our studies for a generation mechanism of the interactions with other molecules in the asphalt (product from distillation of petroleum). Chemical composition and physical properties of the asphalt vary, according to the crude oil source, the manufacturing processes, as well as other ingredients (such as additives and modifiers). Asphalt primarily contains cyclic alkanes, aliphatic compounds, aromatic hydrocarbons, and heterocyclic compounds containing oxygen, nitrogen, and sulfur atoms. These PAHs and their derivatives can migrate in the environment, for example, from contaminated soils into the ground water.29 Therefore, they can be potential health hazard for human.30

The crystal structure of the fluoranthene and acenaphthene has been described in the literature, *i.a.* by Chakrabarti (1955)31 and later by Hazell *et al.* (1977)32; and by Ehrlich (1957)33 and then by Hazell *et al.* (1985)34, respectively.

The crystal data and final refinement details of the compound **I** and **II** are given in Table I. The molecular structure of the fluoranthene and acenaphthene are illustrated in Fig. 1 (a) and (b), respectively.

Compound **I** crystallizes with eight molecules in the asymmetric unit. The molecules in the unit cell are connected by the weak C-H···π interactions between nearest neighbours. The intermolecular C-H···C interactions exist between carbon atoms of condensed rings of the naphthalene structure nearest neighbouring molecules are shown in Figure 2 (a) (marked blue dashed line). The fluoranthene also contains π···π (C···C) interactions, but they are less dominant in this crystal structure. The C···C distances between neighboring molecules are approximately 3.33 Å (see Fig. 2 (a); red dashed line). Generally, the C···C van der Waals distance of 3.40 Å has been adopted as the reference distance for chemical stability.35 Additionally, it is worth noting that the C···C distances are longer than the 2.6 Å distance observed in crystalline benzene.36 The intermolecular C···C distance is comparable also to the C···C distance of the dibenz(a,h)anthracene (3.37 Å).37

The H···H contacts have been marked green dashed line in Fig. 2 (a). The shortest close contacts between hydrogen atoms have distance approximately 2.37 Å (van der Waals radii for the hydrogen atom is 1.2 Å). Whereas C-H···C contacts have been depictured in the same Fig. 2 (a) as blue dashed line. The shortest C-H···π close contacts have distance approximately 2.80 Å.

The intermolecular close contacts have been likewise substantiated by examination of the Hirshfeld surfaces. However, the fingerprint plots (2D representation of the Hirshfeld surface) provide a quantitative measure of the intermolecular interactions on the surface.28,38 The C···H and H···C intermolecular interactions have been depicted as two characteristic and distinct "spikes" in the two-dimensional fingerprint plot, Fig. 3 (a). The C···H (π···H) interactions (30.8 %) are represented by a spike (di = 1.74 Å, de = 1.75 Å) in the bottom right area of the fingerprint plot (these contacts have been mentioned by the green ellipse; see Fig. 3 (a)). Then the H···C (H···π) interactions (25.1 %) are represented by a spike (di = 1.74 Å, de = 1.75 Å) in the upper left area of the fingerprint plot (contacts are marked by red ellipse). Two small areas, visible on the fingerprint plot (Fig. 3 (b)), are the characteristic of π···π interactions (2.0 %). Besides, presented results showed that the structure of **I** is also dominated by H···H contacts (42.1 %); Fig. 3(c).

 According to the classification of Desiraju & Gavezzotti39, the crystal packing of **I** follows herringbone (HB) motif. The ratio of % C···H to % C···C interactions is equals 27.95 > 4.5.40

Hirshfeld surface analysis was also used for visually analyzing intermolecular interactions in the crystal structure of the acenaphthene. The asymmetric unit of **II** contains four acenaphthene molecules, which are linked by the C-H···π interactions. The intermolecular C-H···C interactions, existing between carbon atoms of condensed rings of the naphthalene structure nearest neighbouring molecules, are shown in Figure 2 (b) (blue dashed line). The shortest C-H···π close contacts have distance approximately 2.90 Å. The percentage of π···H (C-H) interactions provides 39.30 %, and is appreciably lower compare to **I**. The C···H interactions (23.2 %) are represented by the characteristic wing (di = de = 1.66 Å) in the bottom right area of the fingerprint plot, Fig. 4 (a) (contacts are denoted by the green ellipse). Then the H···C contacts (16.0 %) are illustrated by a wing (di = de = 1.66 Å) in the upper left area of the fingerprint plot (contacts are denoted by the red ellipse, see Fig. 4 (a)).

A significant difference between the molecular interactions in **I** and **II** in terms of H···H interactions is also noticeable in the fingerprint plots (see Figs. 3 (c) and 4 (c)). In this case, H···H contacts comprise 60.5 % of the surface area. The shortest close contacts between hydrogen atoms have distance approximately 2.53 Å; see Fig. 2 (b) (green dashed line).

The π···π contacts are almost zero, and they are no significant interactions in the crystal structure of the acenaphthene (C···C contacts make 0.2 % of the surface area). The shortest close contacts between carbon atoms have distance approximately 3.70 Å; see Fig. 2 (b) (red dashed line). The visual analysis of the fingerprint plots (C···H contact) of the other PAHs, *e.g.* naphthalene and anthracene shows, that the acenaphthene is more similar to them, than to fluoranthene.41

According to the method of Lootos & Barbour, the molecules of the acenaphthene are arranged in the herringbone motif. The ratio of % C···H to % C···C is greater than 4.5, and is 196.50.40

It should be also noted, that in the unit cell the molecules of the fluoranthene and acenaphthene are not connected by the hydrogen bonds. This fact has been also justified by the spectroscopic studies.

*IR spectra of the compounds* ***I*** *and* ***II***

The IR spectra of polycrystalline samples of the fluoranthene and acenaphthene, measured at 293 K by the KBr pellet technique, are shown in Fig. 5 (a) and (b), respectively. Additionally, the Raman spectra of **I** and **II** have been also presented in Figs. 5 (a) and (b), respectively. These spectra have been measured at room temperature for polycrystalline samples. The Raman spectra allow for additional identification of the νC-H band positions, which are attributed to the C-H bond stretching vibrations in the molecules.42

Polarized IR spectra of **I** and **II** single crystals measured at 293 K and 77 K, in the frequency ranges of the νC-H bands, are demonstrated in Figure 6 (a) and (b), respectively. The temperature-dependence of the polarized crystalline spectra of the fluoranthene and acenaphthene in the frequency ranges of the νC-H bands is presented in Figure 7 (a) and (b), respectively.

The analysis of the IR and Raman spectra indicated, that the skeletal vibrations of C-C bands in aromatic nucleus are much weaker in the IR spectrum than in the Raman spectrum. These data are also based on the experimental data available in the literature.43

The vibrations of the crystalline acenaphthene can be divided into types: aromatic ring C-H stretching (3071-3036 cm-1), CH2 asymmetric stretching (2937-2914 cm-1), CH2 symmetric stretching (2840 cm-1) (see Fig. 5 (b)), deformation in the plane of CH2 group (~1423 cm-1), aromatic ring stretching (~1616-1593 cm-1) and skeletal vibrations representing C=C stretching (~1370 cm-1). In Fig. 5 (b) have been also shown the C-H bending bands appear in the region 841-749 cm-1 (out-of plane bending), which are very strong. In the case of the crystalline fluoranthene the characteristic IR bands in five regions of the spectrum have been illustrated in Fig. 5 (a) and 6 (a). The main types of vibration are C-H stretching vibration, C=C stretching vibration, C-H out-of plane vibration, C-H bending vibration and lattice vibration.43

Analyzing the IR spectra of monocrystalline samples of the acenaphthene, measured at the different orientation of the electric field vector "E", the incident light on the crystal, can be observed a large variability of some bands intensity; Fig. 6 (b). The νC-H bands (in the frequency range from 3060 to 2836 cm-1) in the spectra of **II** crystals are characterized by the two-branch structure with their unique and relatively simple intensity distribution patterns. The polarized light especially strongly influences the intensity of bands of the C-H bonds stretching vibrations in the molecules. From the results in Figure 6 (b) it can be seen that the longer-wave branch (3060-3040 cm-1) of the band is of relatively high intensity when compared with the shorter-wave band (3061-3075 cm-1) branch properties. These effects are related to the arrangement of the molecules in the unit cell. Two molecules lie in the crystalline plane "bc", and the other two are arranged obliquely to them; Fig. 6 (c). Such an arrangement of the molecules causes that regardless of the type obtained wall, have been excited the C-H vibrations different fragments of the molecules by the polarized light. Therefore, different intensity of the lines in the νC-H bands has been observed in the spectra of the acenaphthene crystals. For example, in the case of the polarization 0° the line 2937 cm-1 of the asymmetric CH2 vibrations has significantly lower intensity compared with the line 2914 cm-1 (Fig. 6 (b)). The opposite phenomenon has been observed for the polarization 90°. It may be noted that the polarization effects are also visible in the some of the bands lying at lower frequencies.

The crystalline IR spectrum of acenaphthene crystals shows, that the temperature decrease till 77 K is responsible for a slight growth of the longer-wave branch intensity. Whereas, the shorter-wave branch intensity remains unchanged; see Fig 7 (b).

 Very similar phenomena have been observed in the spectra of the fluoranthene crystals (Figs. 6 (a) and 7 (a)). In this case, also the largest differences in the intensities of the bands are visible in the frequency range of the C-H bond stretching vibration in the molecules. On the other hand, the differences between the spectra measured at room temperature and the temperature of liquid nitrogen are a result of stiffening molecules. Therefore, it is discernible sharpening of the νC-H bands contour, as well as a slight growth of their intensity.

*DFT calculation results for the compounds* ***I*** *and* ***II***

Our studies have shown satisfactory correlation between calculated and experimental structural parameters (XRD) (Tables II and III). The significant differences in the DFT and XRD geometries have been observed in the case of the fluoranthene in the C8-C9-C10-C1, C24-C25-C26-C17, C2-C1-C10-C9, C18-C17-C26-C25, C27-C25-C26-C21 and C32-C17-C26-C21 torsion angles, which have values -178.5°, -179.3°, -179.5°, -178.1°, -178.7° and 179.1°, respectively. While those calculated values by the DFT method for the first five torsion angles are ~ 180.00° and the last one amount approximately -180.00° (see Table II).

Figure 8 (a) and (b) demonstrate the comparison of the calculated IR spectra of the fluoranthene and acenaphthene, respectively. It should be noted that the theoretical model satisfactorily reproduced the experimental infrared spectra for both the PAHs.

CONCLUSIONS

In the present paper, the crystal structure, the DFT calculations, analysis of the Hirshfeld surfaces and fingerprint plots, as well as spectroscopic properties of the title PAHs are reported.

These results show that the Hirshfeld surface and fingerprint plot analysis provides rapid quantitative insight into the intermolecular interactions in the molecular solids. The close contacts, in the case of both analyzed compounds, are dominated by H···C (C-H···π) and H···H contacts and these relatively weak interactions have evident signatures in the fingerprint plots. In addition, it should be emphasized that the analysis of the Hirshfeld surface is good correlated to the spectroscopic studies. Also the comparison of the DFT model with XRD in the present study may be considered a good.

Based on these conclusions, further our advisement concerning the generation mechanism of the interactions with other molecules in the asphalt will be continued.

SUPPLEMENTARY DATA

CCDC-1011192 and CCDC-1011193 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk

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