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ORIGINAL RESEARCH

# Friedel–Crafts acyl rearrangements in the fluoranthene series

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**Abstract** Friedel–Crafts monoacylation and diacylation of fluoranthene (FT) gave 3-acetyl-, 8-acetyl-, 3-benzoyl-, 8-benzoyl-, 3-(4-fluorobenzoyl)-, 8-(4-fluorobenzoyl)-, 3,9-diacetyl-, 3,9-dibenzoyl-, and 3,9-bis(4-fluorobenzoyl)fluoranthene (3-AcFT, 8-AcFT, 3-BzFT, 8-BzFT, 3-(4-FBz)FT, 8-(4-FBz)FT, 3,9-$Ac_2$FT, 3,9-$Bz_2$FT, and 3,9-$(4\text{-FBz})_2$FT). The crystal and molecular structures of 8-AcFT, 3,9-$Ac_2$FT, 7,10-$Ac_2$FT, 3-BzFT, 8-BzFT, and 3-(4-FBz)FT were determined by X-ray crystallography. The structures of the fluoranthene derivatives, including 3,9-$Ac_2$FT were verified by $^1$H-, $^{13}$C-, and $^{19}$F-NMR spectroscopy. The Friedel–Crafts acyl rearrangements in PPA of the above fluoranthene derivatives were studied at various temperatures and times. The kinetically controlled product 3-AcFT/3-BzFT rearranged to the thermodynamically-controlled product 8-AcFT/8-BzFT, not vice versa. 3,9-$Ac_2$FT, 3,9-$Bz_2$FT, and 3,9-$(4\text{-FBz})_2$FT underwent deacylation in PPA to give 8-AcFT, 8-BzFT, and 8-(4-FBz)FT, respectively. Deacetylation of 3,9-$Ac_2$FT gave also 3-methyl-1*H*-benzo[*cd*]fluoranthene (3-MeBcdFT). The rich Friedel–Crafts acylation chemistry in PPA revealed in the fluoranthene series is characterized by regioselectivity. DFT calculations at B3LYP/6-31G(*d*) supported the regioselectivity including the formation of 3,9-$Ac_2$FT, and the win of kinetic control over thermodynamic control.

**Keywords** X-ray crystallography · NMR spectroscopy · Regioselectivity · Deacylation · Kinetic control · Thermodynamic control · PPA · DFT

## Introduction

Friedel–Crafts alkylation and Friedel–Crafts acylation are considered cornerstones of organic chemistry [1, 2]. For many years, it has been accepted that Friedel–Crafts acylations, in contrast to Friedel–Crafts alkylations, are usually irreversible, free of rearrangements, and isomerizations [1, 3, 4]. The difference in behavior between Friedel–Crafts acylation and Friedel–Crafts alkylation was attributed to the resonance stabilization existing between the acyl group and the aromatic nucleus [5], which may serve as a barrier against rearrangements and reversible processes. When the acyl group has been tilted out of the plane of the aromatic nucleus, e.g., by neighboring bulky substituents, the resonance stabilization was reduced and the pattern of irreversibility of Friedel–Crafts has been challenged [5–7].

In 1955, Gore introduced the concept of reversibility of Friedel–Crafts acylation, proposing that "The Friedel–Crafts acylation reaction of reactive aromatic hydrocarbons is a reversible process" [8]. Gore concluded that "Reversibility is an important factor in acylation reactions" [8]. In 1964, Gore argued that in polycyclic aromatic systems other than naphthalene, there is

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This contribution is dedicated to Professor George A. Olah, the illustrious scientist, the Doyen of Friedel–Crafts chemistry, in celebration of his forthcoming 90th birthday.

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direct experimental evidence in favor of reversibility [9]. The reversibility studies have been focused mainly on unusual aspects of selectivity, including deacylations, one-way rearrangements, and kinetic versus thermodynamic control [7]. The incursion of reversibility in Friedel–Crafts acylations was revealed by Agranat, et al., in the benzoylation of naphthalene in polyphosphoric acid (PPA) at elevated temperatures [10]. The kinetically controlled 1-benzoylnaphthalene (1-BzNA) rearranged to the thermodynamically controlled 2-benzoylnaphthalene (2-BzNA) in PPA at 140 °C (vide infra), whereas 2-BzNA underwent only deacylation, e.g., at 140 °C, to give naphthalene (NA).

The reversibility concept was applied to the synthesis of new linearly annelated polycyclic aromatic ketones, by intramolecular Friedel–Crafts acyl rearrangements of their angularly annelated constitutional isomers [11–13]. Complete reversibility of Friedel–Crafts acylation was established in the intramolecular *ortho–para* acyl rearrangements of 1-fluorofluorenone ⇌ 3-fluorofluorenones in PPA [14].

Acyl rearrangements and reversibility in Friedel–Crafts acylations have been associated with thermodynamic control [6, 14]. Frangopol et al. [15] and Nenitzescu and Balaban [16, 17] have reported the reversibility of Friedel–Crafts acetylation of olefins.

The contributions of kinetic control versus thermodynamic control in Friedel–Crafts acyl rearrangements remain an open question, in spite of the rich chemistry of Friedel–Crafts acylations [3, 8, 9]. We have recently reported that kinetic control wins out over thermodynamic control in the Friedel–Crafts acyl rearrangements of diacetylanthracenes in PPA [18] and non-planarity of the PAKs is not a sine qua non condition for the rearrangements as in case of dibenzofluorenone [19]. The conformational variations in these PAKs, which contribute to the understanding of the motifs of reversibility, have been described [20, 21].

We report here the results of a study of the Friedel–Crafts acyl rearrangements of acylfluoranthenes which includes mono- and diacetylfluoranthenes, mono- and dibenzoylfluoranthenes, and mono and bis(4-fluorobenzoyl)fluoranthenes in PPA.

## Experimental section

Melting points were uncorrected. NMR spectra were recorded with Bruker Avance II 500 and AMX 400 spectrometers; $^1$H-NMR spectra were recorded at 500.2 and 400.13 MHz in $CDCl_3$ as a solvent and as an internal standard, δ($CHCl_3$) = 7.260 ppm. $^{13}$C-NMR spectra were recorded at 125.78 MHz using $CDCl_3$ as solvent and as internal standard, δ($CDCl_3$) = 77.01 ppm, $^{19}$F-NMR spectra were recorded at 470.66 MHz in $CDCl_3$ as a solvent and as an internal standard, δ($CHCl_3$) = 7.260 ppm and referenced and reported according to IUPAC Recommendations 2008 [22]. For comparison, the $^{19}$F-NMR chemical shift of fluorobenzene in $CDCl_3$ is −113.06 ppm. Complete assignments were carried out through 2D correlation spectroscopy (COZY, NOESY, HSQC, and HMBC) and recorded at 500.2 MHz. IR spectra were recorded using ALPHA Bruker FTIR spectrometer with an OPUS program using KBr. UV-Visible spectra were recorded with a Varian UV-Visible spectrophotometer using $CHCl_3$ as solvent and as internal standard. Column chromatography was performed using silica gel 60 (0.063–0.2 mm, 70–230 mesh ASTM) and appropriate solvents, the silica gel was obtained from Merck KGaA, Darmstadt, Germany. Mass spectra, LC-MS, spectra were recorded with Accurate-Mass Q-TOF LC-MS from Quaternary Agilent technologies using acetonitrile or $CHCl_3$ as a solvent. Elementary analyses for new polycyclic aromatic ketones (PAKs) were carried out using Perkin Elemer Preciesly, Series II, CHNS/O analyzer. LC-MS and Elementary analyses were carried out by Dr. Carina Hazan, the microanalysis laboratory, Institute of Chemistry, The Hebrew University of Jerusalem. TLC $R_f$ on silica gel 60 $F_{254}$ plates was carried out using PE (40–60 °C)/EtOAc 80:20 as eluent. PLC chromatography on silica gel 60 $F_{254}$ plates was obtained from E. Merck.

Fluoranthene (98%), benzoyl chloride, 4-fluorobenzoyl chloride, acetyl chloride, $AlCl_3$, and polyphosphoric acid (PPA; 84% weight of $P_2O_5$, density 1.9 g/ml) were obtained from Acros Organics, Israel. All the solvents AR grades were obtained from Bio-Lab Ltd., Israel. 7,10-diacetylfluoranthene (7,10-$Ac_2$FT) was obtained from Akos Consulting and Solutions Deutschland GmbH, Germany. Chloroform, dichloromethane and 1,2-dichloroethane were dried on $CaCl_2$.

### *X-ray crystallography*

Single crystal of each fluoranthene derivative was attached to a 400/50 MicroMeshes™ with NVH Oil [23], and transferred to a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite-monochromator. Maintaining the temperature at 173 K was done with a Bruker KRYOFLEX nitrogen cryostat. The system was controlled by a Pentium-based PC running the SMART software package [24]. Data were collected at room temperature for 8-acetylfluoranthene (8-AcFT), and at 173 K for the other fluoranthene derivatives under study, using MoKα radiation ($\lambda$ = 0.71073 Å). Immediately after collection, the raw data frames were transferred to a second PC computer for integration and reduction by the SAINT program package [25]. The structures were solved and refined by the SHELXTL software package [26].

### *Quantum mechanical calculations*

The quantum mechanical calculations of the fluoranthene derivatives under study were performed with the Gaussian 09 [27] packages. Becke's three-parameter hybrid density functional B3LYP [28], with the non-local correlation functional of Lee et al. [29] was used. The Pople style split valence 6-31G(*d*) basis set was employed for geometry optimizations. All structures were fully optimized, using symmetry constrains as indicated. Vibration frequencies were calculated at B3LYP/6-31G(*d*) to verify the nature of the stationary points. Non-scaled thermal corrections to enthalpy and to free-energy calculated at the same levels were applied. Calculations in the solvent reaction field (SCRF) were performed using the polarizable continuum model (PCM) with formic acid as solvent, as implemented in Gaussian 09 [30].

### *Procedures*

8-Acetylfluoranthene (8-AcFT) and 3-acetylfluoranthene (3-AcFT) were prepared according to a literature procedure [31] with slight modifications. Fluoranthene (10 g, 49 mmol) was dissolved in dry $CH_2Cl_2$ and treated with acetyl chloride (4.4 ml, 64 mmol). The reaction mixture was cooled to 0 °C. $AlCl_3$ (8.5 g, 64 mmol) was then added in one portion. The reaction mixture was stirred for 1 h in ice bath then 4 h at rt. The complex was decomposed with cold dilute aqueous HCl (or cold $H_2O$). The reaction product was extracted with $CH_2Cl_2$, washed with $H_2O$ and $NaHCO_3$(aq), dried over $MgSO_4$, and the organic solvent was evaporated under reduced pressure. The resulting crude product (7.0 g) contained 3-AcFT and 8-AcFT in the ratio of 35:65. Column chromatography of the crude product on silica gel using PE/EtOAc 99:1% as eluent gave the first fraction, 2.0 g of 3-AcFT, yield 17.0%, mp. 128–129 °C (lit. 127–129 °C [31, 32]); TLC $R_f = 0.60$. The second fraction contained 8-AcFT, 3.0 g, yield 25.0%, mp. 102–103 °C (lit. 101–102 °C [31–33]), TLC $R_f = 0.51$. A single crystal of 8-AcFT was obtained by recrystallization from EtOAc.

**3-AcFT** $^{1}$H-NMR δ($CDCl_3$, ppm)—8.77 (d, $^{3}J = 8.5$ Hz, 1H, H$^{4}$), 8.17 (d, $^{3}J = 7.5$ Hz, 1H, H$^{2}$), 7.91 (d, $^{3}J = 8.0$ Hz, 1H, H$^{1}$), 7.89–7.88 (m, 2H, H$^{6}$, H$^{10}$), 7.86 (dd, $^{3}J = 7.5$ Hz, $^{4}J = 1.0$ Hz, $^{5}J = 0.5$ Hz, 1H, H$^{7}$), 7.68 (td, $^{3}J = 6.5$ Hz, $^{3}J = 7.0$ Hz, $^{4}J = 2.0$ Hz, 1H, H$^{5}$), 7.43 (td, $^{3}J = 7.5$ Hz, $^{3}$ $J = 7.25$ Hz, $^{4}J = 1.5$ Hz, 1H, H$^{8}$), 7.35 (td,$^{3}J = 7.5$ Hz, $^{3}J = 7.25$ Hz, $^{4}J = 1.5$ Hz, 1H, H$^{9}$), and 2.79 (s, 3H, $CH_3$). $^{13}$C-NMR δ($CDCl_3$, ppm)—200.4 (C$^{11}$), 141.9 (C$^{10b}$), 140.6 (C$^{6b}$), 138.1 (C$^{10a}$), 137.0 (C$^{6a}$), 133.8 (C$^{3}$), 133.0 (C$^{10c}$), 132.0 (C$^{2}$), 130.2 (C$^{5}$), 128.9 (C$^{10}$), 127.9 (C$^{3a}$), 127.8 (C$^{7}$), 127.1 (C$^{4}$), 122.3 (C$^{8}$), 121.6 (C$^{9}$), 120.6 (C$^{6}$), 118.5 (C$^{1}$), and 29.1 ($CH_3$).

**8-AcFT** $^{1}$H-NMR δ($CDCl_3$, ppm)—8.49 (s, 1H, H$^{7}$), 8.02 (2d, $^{3}J = 7.0$ Hz, 2H, H$^{1}$, H$^{6}$), 7.99 (dd, $^{3}J = 8.5$ Hz, $^{4}J = 1.5$ Hz, 1H, H$^{9}$), 7.95 (d, $^{3}J = 8.0$ Hz, 1H, H$^{10}$), 7.92 (d, $^{3}J = 8.0$ Hz, 1H, H$^{3}$), 7.89 (d, $^{3}J = 8.0$ Hz, 1H, H$^{4}$), 7.68 (t, $^{3}J = 7.5$ Hz, $^{3}$ $J = 7.5$ Hz, 2H, H$^{2}$, H$^{5}$), and 2.71 (s, 3H, $CH_3$). $^{13}$C-NMR δ($CDCl_3$, ppm)—197.9 (C$^{11}$), 143.6 (C$^{10a}$), 139.6 (C$^{3a}$), 136.6 (C$^{6b}$), 136.0 (C$^{6a}$), 135.7 (C$^{8}$), 133.2 (C$^{10c}$), 129.6 (C$^{10b}$), 128.3 (C$^{2}$), 128.2 (C$^{9}$), 128.1 (C$^{10}$), 127.9 (C$^{3}$), 127.2 (C$^{4}$), 121.4 (C$^{1}$), 121.2 (C$^{6}$), 121.2 (C$^{7}$), 120.8 (C$^{5}$), and 26.8 ($CH_3$).

**3,9-Diacetylfluoranthene (3,9-Ac$_2$FT)** was prepared according to a literature procedure [31] with slight modifications. To a cooled solution of fluoranthene (10 g, 49 mmol) in dry $CH_2Cl_2$ (150 ml) at 0 °C, acetyl chloride (6.4 ml, 99.0 mmol) and then $AlCl_3$ (17.8 g, 128.3 mmol) were added. The reaction mixture was stirred for 1 h at 0 °C and then for 4 h at RT. The work-up was carried out according to the procedure described above. Column chromatography on silica gel of the crude product using PE/EtOAc 98:2 as eluent gave 6 g of pure 3,9-Ac$_2$FT, yield 42%, mp. 139–140 °C (lit 137–139 °C [31, 34]), TLC $R_f = 0.26$. A single crystal of 3,9-Ac$_2$FT was obtained by recrystallization from EtOH.

$^{1}$H-NMR δ($CDCl_3$, ppm)—8.86 (dd, $^{3}J = 8.5$ Hz, $^{5}J = 0.5$ Hz, 1H, H$^{4}$), 8.48 (s, 1H, H$^{10}$), 8.22 (d, $^{3}J = 7.0$ Hz, 1H, H$^{2}$), 8.03 (dd, $^{3}J = 7.75$ Hz, $^{4}J = 2.0$ Hz, $^{4}J = 1.5$ Hz, 1H, H$^{8}$), 8.00 (d,$^{3}J = 7.5$ Hz, 1H, H$^{1}$), 7.98 (dd, $^{3}J = 7.0$ Hz, $^{4}J = 1.0$ Hz, 1H, H$^{6}$), 7.92 (dd, $^{3}J = 9.0$ Hz, $^{5}J = 0.5$ Hz, 1H, H$^{7}$),7.74 (dd, $^{3}J = 8.0$ Hz, $^{4}J = 2.0$ Hz, 1H, H$^{5}$), 2.80 (s, 3H, $^{3}CH_3$), and 2.71 (s, 3H, $^{9}CH_3$). $^{13}$C-NMR δ($CDCl_3$, ppm)—200.4 (C$^{13}$), 197.6 (C$^{11}$), 144.7 (C$^{10a}$), 140.8 (C$^{10b}$), 138.3 (C$^{3}$), 136.5 (C$^{8}$), 135.7 (C$^{6a}$), 134.1 (C$^{6b}$), 133.8 (C$^{10c}$), 132.2 (C$^{2}$), 130.3 (C$^{5}$), 129.6 (C$^{9}$), 128.5 (C$^{4}$), 127.9 (C$^{3a}$), 122.0 (C$^{1}$), 121.9 (C$^{7}$), 121.3 (C$^{10}$), 119.4 (C$^{6}$), 29.1 (C$^{3}$H$_3$), and 26.9 (C$^{9}$H$_3$).

8-Benzoylfluoranthene (8-BzFT) and 3-benzoylfluoranthene (3-BzFT) were prepared according to a literature procedure [32] with slight modifications. To a solution of fluoranthene (10 g, 49 mmol) at 0 °C in dry $CH_2Cl_2$ (150 ml), benzoyl chloride (7.5 ml, 64 mmol) was added followed by $AlCl_3$ (8.5 g, 64 mmol). The reaction mixture was left with stirring at 0 °C for 1 h then at RT for 4 h. The work-up was carried out according to the procedure described above. The crude product which consisted of a mixture of 3-BzFT and 8-BzFT in the ratio of 18:25, were subjected to column chromatography on silica gel using PE/EtOAc 99:1 as eluent. The first fraction was collected to give 2.5 g of 3-BzFT, yield 17.0%, mp. 130–131 °C (lit. 129–130 °C [32]), TLC $R_f = 0.69$. The second fraction contained 3 g of 8-BzFT, yield 25.0% mp. 120–121 °C (lit. 120–121 °C [32]); TLC $R_f = 0.49$. Single crystals of 8-BzFT and 3-BzFT were obtained by recrystallizations from EtOAc and $CHCl_3$, respectively.

**3-BzFT** $^{1}$H-NMR δ($CDCl_3$, ppm)—8.17 (d, $^{3}J = 8.5$ Hz, 1H, H$^{4}$), 7.95 (dd, $^{3}J = 7.5$ Hz, $^{4}J = 3.0$ Hz, 2H, H$^{1}$, H$^{6}$), 7.93–7.92 (m, H$^{7}$, H$^{10}$), 7.89 (d, $^{3}J = 7.5$ Hz, 2H, H$^{2'}$, H$^{6'}$), 7.85 (d,$^{3}J = 7.0$ Hz, 1 Hz, H$^{2}$), 7.66 (td, $^{3}J = 7.5$ Hz, $^{4}J = 1.5$ Hz, 1H, H$^{5}$), 7.62 (t, $^{3}J = 7.0$ Hz, $^{3}J = 7.5$ Hz, 1H, H$^{4'}$), 7.45 (t, $^{3}J = 7.5$, $^{3}J = 8$ Hz, 2H, H$^{3'}$, H$^{5'}$), 7.44 (td, $^{3}J = 7.25$ Hz, $^{3}J = 8.5$ Hz, $^{4}J = 1.5$ Hz, 1H, H$^{8}$), and 7.40 (td, $^{3}J = 8.5$ Hz, $^{3}J = 7.5$ Hz, 1 Hz, H$^{9}$). $^{13}$C-NMR δ($CDCl_3$, ppm)—197.2 (C$^{11}$), 140.6 (C$^{10b}$), 140.3 (C$^{6b}$), 138.8 (C$^{1'}$), 136.5 (C$^{10a}$), 137.1 (C$^{6a}$), 132.9 (C$^{10c}$), 132.9 (C$^{4'}$), 132.7 (C$^{3}$), 131.8 (C$^{2}$), 130.4 (C$^{2'}$, C$^{6'}$), 129.5 (C$^{5}$), 128.7 (C$^{8}$), 128.5 (C$^{3a}$), 128.4 (C$^{3'}$, C$^{5'}$), 127.8(C$^{9}$), 126.0 (C$^{4}$), 122.2 (C$^{10}$), 121.7 (C$^{7}$), 120.7 (C$^{6}$), and 118.4 (C$^{1}$).

**8-BzFT** $^{1}$H-NMR δ(CDCl$_3$, ppm)—8.40 (s, 1H, H$^{7}$), 8.07 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{6}$), 8.02 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{1}$), 8.01 (d, $^{3}J$ = 8.0 Hz, 1H, H$^{10}$), 7.95 (d, $^{3}J$ = 8.5 Hz, 1H, H$^{4}$), 7.92 (d, $^{3}J$ = 8.5 Hz, 1H, H$^{3}$), 7.89 (2d, $^{3}J$ = 7.5 Hz, 2H, H$^{2'}$, H$^{6'}$), 7.86 (dd, $^{3}J$ = 8.5 Hz, $^{4}J$ = 1.5 Hz, 1H, H$^{9}$), 7.71 (t, $^{3}J$ = 7.5 Hz, $^{3}J$ = 8.5 Hz, 1H, H$^{5}$), 7.69 (t, $^{3}J$ = 8.5 Hz, $^{3}J$ = 8.5 Hz, 1H, H$^{2}$), 7.63 (t, $^{3}J$ = 7.5 Hz, $^{3}J$ = 7.5 Hz, 1H, H$^{4'}$), and 7.54 (t, $^{3}J$ = 7.5 Hz, $^{3}J$ = 7.5 Hz, 2H, H$^{3'}$, H$^{5'}$). $^{13}$C-NMR δ(CDCl$_3$, ppm)—196.7(C$^{11}$), 143.2 (C$^{10a}$), 139.4 (C$^{6b}$), 138.1 (C$^{1'}$), 136.7 (C$^{8}$), 136.1 (C$^{10b}$), 135.8 (C$^{6a}$), 133.2 (C$^{10c}$), 132.3 (C$^{4'}$), 130.2 (C$^{9}$), 130.1 (C$^{3a}$), 130.0 (C$^{2'}$, C$^{6'}$), 128.3 (C$^{3'}$,C$^{5'}$), 128.3 (C$^{2}$), 128.2 (C$^{5}$), 127.9 (C$^{4}$), 127.3 (C$^{3}$), 123.2 (C$^{7}$), 121.5 (C$^{6}$), 121.0 (C$^{10}$), and 120.9 (C$^{1}$).

**3,9-Dibenzoylfluoranthene (3,9-Bz$_2$FT)** A suspension of AlCl$_3$ (3.5 g, 26.4 mmol) and benzoyl chloride (3.1 ml, 26.4 mmol) in dry ClCH$_2$CH$_2$Cl (150 ml) was heated to 80 °C. 8-BzFT (3.0 g, 10.7 mmol) was then added, and the reaction was stirred overnight at 80 °C. The work-up was carried out according to the procedure described above. Column chromatography on silica gel of the crude product using PE/EtOAc 99:1 as eluent gave 1.0 g of 3,9-dibenzoylfluoranthene (3,9-Bz$_2$FT) as a pale yellow powder, yield 22.0%, mp. 159–160 °C, TLC $R_f$ = 0.49. Elementary analysis: calculated for C$_{30}$H$_{18}$O$_2$: C = 87.78% and H = 4.42%. Found: C = 87.37%, H = 4.34%. MS, *m/z* = 411.138 (M$^{+1}$); IR: $\nu$ = 1653.18 cm$^{-1}$ (C=O); UV/vis (nm): $\lambda$ = 391, 368, and 328.

$^{1}$H-NMR δ(CDCl$_3$, ppm)—8.46 (s, 1H, H$^{10}$), 8.26 (d, $^{3}J$ = 8.5 Hz, 1H, H$^{4}$), 8.06 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{6}$), 8.01 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{1}$), 8.00 (d, $^{3}J$ = 7.5 Hz, 1H, H$^{7}$), 7.91–7.78 (m, 6H, H$^{2}$, H$^{8}$, H$^{2'}$, H$^{2''}$, H$^{6'}$, H$^{6''}$), 7.72 (td, $^{3}J$ = 8.0 Hz, $^{4}J$ = 1.5 Hz, 1H, H$^{5}$), 7.64 (td, $^{3}J$ = 8.5 Hz, $^{3}J$ = 6.5 Hz, $^{4}J$ = 1.5 Hz, $^{4}J$ = 1.0 Hz, 2H, H$^{4'}$, H$^{4''}$), 7.52 (t, $^{3}J$ = 7.25 Hz, $^{3}J$ = 8.0 Hz, 2H, H$^{3'}$, H$^{3''}$), 7.51 (t, $^{3}J$ = 7.0 Hz, $^{3}J$ = 8.5 Hz, 2H, H$^{5'}$, H$^{5''}$). $^{13}$C-NMR δ(CDCl$_3$, ppm)—196.9 (C$^{13}$), 196.5 (C$^{11}$), 143.9 (C$^{10a}$), 139.5 (C$^{10b}$), 138.5 (C$^{1''}$), 138.5 (C$^{10c}$), 137.9 (C$^{1'}$), 137.0 (C$^{8}$), 135.9 (C$^{6a}$), 135.5 (C$^{3}$), 133.5 (C$^{6b}$), 133.1 (C$^{4'}$), 132.4 (C$^{4''}$), 131.8 (C$^{2}$), 131.2 (C$^{9}$), 130.4 (C$^{2'}$, C$^{6'}$), 130.0 (C$^{2''}$, C$^{6''}$), 129.6(C$^{5}$), 128.5 (C$^{3a}$), 128.5 (C$^{3'}$, C$^{5'}$), 128.4 (C$^{3''}$, C$^{5''}$), 127.2 (C$^{4}$), 123.7 (C$^{7}$), 122.1 (C$^{6}$), 121.2 (C$^{10}$), and 119.3 (C$^{1}$).

**3-(4-Fluorobenzoyl)fluoranthene (3-(4-FBz)FT) and 8-(4-fluorobenzoyl)fluoranthene (8-(4-FBz)FT)** Fluoranthene (10.0 g, 49 mmol) was dissolved in dry CH$_2$Cl$_2$ (150 ml) and treated with 4-fluorobenzoyl chloride (10.1 ml, 68 mmol); the reaction mixture was cooled to 0 °C, AlCl$_3$ (8.6 g, 64 mmol) was then added in one portion. The reaction mixture was left with stirring for 1 h in 0 °C then for 4 h at rt. The precipitate was filtered off and both the filtrate and the precipitate were decomposed using cold dilute aqueous HCl. The crude product from the precipitate was recrystallized from PE to give 8-(4-fluorobenzoyl)fluoranthene (8-(4-FBz)FT), 3.5 g, yield 22.0%, mp. 143–144 °C, TLC $R_f$ = 0.74. A single crystal 8-(4-FBz)FT was obtained by recrystallization from EtOAc. Elementary analysis: calculated for 8-(4-FBz)FT (C$_{23}$H$_{13}$FO): C = 84.45%, H = 3.95%, F = 6.15%; found: C = 84.24%, H = 3.99%, F = 5.30%. MS: *m/z* = 325 (M$^{+1}$); IR, 1645.61 cm$^{-1}$ (C=O); UV/VIS (nm): 385, 368 and 327. The crude product from the filtrate was subjected to column chromatography on silica gel using PE/EtOEt 99:1 to give 2.5 g of 3-(4-fluorobenzoyl)fluoranthene (3-(4-FBz)FT) as a yellow powder, yield 17.0%, mp. 187.8–188.5 °C; TLC $R_f$ = 0.71. A single crystal of 3-(4-FBz)FT was obtained by recrystallization from EtOAc. Elementary analysis: calculated for 3-(4-FBz)FT (C$_{23}$H$_{13}$FO): C = 85.17%, H = 4.04% and F = 5.86%; found: C = 84.24%, H = 3.99% and F = 5.30%. MS, *m/z* = 325(M$^{+1}$); IR: $\nu$ = 1641.55 cm$^{-1}$ (C=O); UV/vis (nm): $\lambda$ = 392, 368, and 338.

**3-(4-FBz)FT** $^{1}$H-NMR δ(CDCl$_3$, ppm)—8.10 (d, $^{3}J$ = 8.5 Hz, 1H, H$^{4}$), 7.95 (2d, $^{3}J$ = 7.0 Hz, 2H, H$^{1}$, H$^{6}$), 7.93 (d, $^{3}J$ = 6.0 Hz, 2H, H$^{2'}$, H$^{6'}$), 7.89 (d, $^{3}J$ = 9.5 Hz, 2H, H$^{8}$, H$^{9}$), 7.82 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{2}$), 7.65 (td, $^{3}J$ = 6.5 Hz, $^{4}J$ = 2.0 Hz, 1H, H$^{5}$), 7.44 (td, $^{3}J$ = 8.0 Hz, $^{3}J$ = 7.0 Hz, $^{4}J$ = 1.0 Hz, $^{4}J$ = 1.5 Hz, $^{4}J$ = 2.0 Hz, 1H, H$^{7}$), 7.41 (td, $^{3}J$ = 8.0 Hz, $^{3}J$ = 8.0 Hz, $^{4}J$ = 1.0 Hz, $^{4}J$ = 1.5 Hz, $^{4}J$ = 2.0 Hz, 1H, H$^{10}$), and 7.17 (t, $^{3}J$ = 7.5 Hz, $^{3}J$ = 7.5 Hz, 2H, H$^{3'}$, H$^{5'}$). $^{13}$C-NMR δ(CDCl$_3$, ppm)—195.5 (C$^{11}$), 165.7 (C$^{4'}$), 140.7 (C$^{10b}$), 140.3 (C$^{10a}$), 138.5 (C$^{6b}$), 137.2 (C$^{6a}$), 135.1 (C$^{1'}$), 134.8 (C$^{10c}$), 133.0 (C$^{2'}$, C$^{6'}$), 132.8 (C$^{3}$), 131.4 (C$^{2}$), 129.5 (C$^{5}$), 128.7 (C$^{7}$), 128.4 (C$^{3a}$), 127.9 (C$^{10}$), 125.8 (C$^{4}$), 122.2 (C$^{9}$), 121.7 (C$^{8}$), 120.8 (C$^{6}$), 118.4 (C$^{1}$), and 115.7 (C$^{3'}$, C$^{5'}$). $^{19}$F-NMR δ(CDCl$_3$, ppm)—−105.26.

**8-(4-FBz)FT** $^{1}$H-NMR δ(CDCl$_3$, ppm)—8.36 (s, 1H, H$^{7}$), 8.07 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{1}$), 8.02 (d, $^{3}J$ = 6.5 Hz, 1H, H$^{6}$), 8.01 (d, $^{3}J$ = 7.5 Hz, 1H, H$^{10}$), 7.95 (2d, $^{3}J$ = 8.0 Hz, 2H, H$^{3}$, H$^{4}$), 7.92 (dd, $^{3}J$ = 7.0 Hz, $^{4}J$ = 1.5 Hz, 2H, H$^{3'}$, H$^{5'}$), 7.82 (dd, $^{3}J$ = 7.0 Hz, $^{4}J$ = 1.5 Hz, 1H, H$^{9}$), 7.71 (t, $^{3}J$ = 8.0 Hz, $^{3}J$ = 8.0 Hz, 1H, H$^{2}$), 7.69 (t, $^{3}J$ = 8.0 Hz, $^{3}J$ = 8.0 Hz, 1H, H$^{5}$), and 7.21 (t, $^{3}J$ = 8.5 Hz, $^{3}J$ = 8.5 Hz, 2H, H$^{2'}$, H$^{6'}$). $^{13}$C-NMR δ(CDCl$_3$, ppm)—195.3 (C$^{11}$), 165.4 (C$^{4'}$), 143.3 (C$^{10a}$), 139.5 (C$^{6b}$), 136.6 (C$^{8}$), 136.0 (C$^{6a}$), 135.8 (C$^{10b}$), 134.3 (C$^{1'}$), 133.2 (C$^{10c}$), 132.6 (C$^{3'}$, C$^{5'}$), 130.1 (C$^{3a}$), 130.0 (C$^{9}$), 128.3 (C$^{5}$), 128.2 (C$^{2}$), 128.0 (C$^{3}$), 127.4 (C$^{4}$), 123.0 (C$^{7}$), 121.5 (C$^{1}$), 121.1 (C$^{10}$), 121.0 (C$^{6}$), and 115.6 (C$^{2'}$, C$^{6'}$). $^{19}$F-NMR δ(CDCl$_3$, ppm)—−106.25.

**3,9-Bis(4-fluorobenzoyl)fluoranthene (3,9-(4-FBz)$_2$FT)** To a suspension of AlCl$_3$ (3.3 g, 26.4 mmol) and 4-fluorobenzoyl chloride (3.9 ml, 25 mmol) in dry ClCH$_2$CH$_2$Cl (150 ml) at 80 °C, 8-(4-FBz)FT (3.0 g, 9.3 mmol) was added. The reaction was stirred at 80 °C overnight. The work-up was carried out according to the procedure described above. Column chromatography on silica gel of the crude product using PE/EtOAc 99:1 gave 0.67 g of 3,9-bis(4-fluorobenzoyl)fluoranthene (3,9-(4-FBz)$_2$FT) as a pale yellow powder, yield 15.0%, mp. 184.1–

185.5 °C. TLC $R_f$ = 0.59. Single crystal of 3,9-(4-FBz)$_2$FT was obtained by recrystallization from CDCl$_3$. Elementary analysis: calculated for 3,9-(4-FBz)$_2$FT ($C_{30}H_{11}F_2O_2$): C = 80.71, H = 3.61 and F = 8.51%; found: C = 80.19, H = 3.60 and F = 8.00%. MS: *m/z* = 446.11(M$^{+1}$); IR: $\nu$ = 1646.92 cm$^{-1}$ (C=O); UV/vis (nm): $\lambda$ = 383, 368, and 316.

$^{1}$H-NMR δ(CDCl$_3$, ppm)—8.389 (s, 1H, H$^{10}$), 8.21 (d, $^{3}J$ = 8.5 Hz, 1H, H$^{4}$), 8.08 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{6}$), 8.03 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{1}$), 8.02 (d, $^{3}J$ = 7.5 Hz, 1H, H$^{7}$), 7.99–7.92 (m, 4H, H$^{2'}$, H$^{6'}$, H$^{2''}$,H$^{6''}$), 7.86 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{2}$), 7.86 (dd, $^{3}J$ = 7.5 Hz, $^{4}$ $J$ = 1.5 Hz, 1H, H$^{8}$), 7.73 (td, $^{3}J$ = 7.75 Hz, $^{3}$ $J$ = 7.5 Hz, $^{4}$ $J$ = 1.5 Hz, 1H, H$^{5}$), 7.22 (t, $^{3}J$ = 8.5 Hz, $^{3}$ $J$ = 8.5 Hz, 2H, H$^{3''}$, H$^{5''}$), and 7.19 (t, $^{3}J$ = 8.5 Hz, $^{3}$ $J$ = 9.0 Hz, 2H, H$^{3'}$, H$^{5'}$). $^{13}$C-NMR δ(CDCl$_3$, ppm)—195.2(C$^{11}$), 194.9(C$^{13}$), 166.6 (C$^{4'}$), 164.6 (C$^{4''}$), 143.8 (C$^{10a}$), 139.4 (C$^{10b}$), 138.4 (C$^{3}$), 136.8 (C$^{8}$), 135.8 (C$^{6a}$), 135.3 (C$^{6b}$), 134.8 (C$^{1''}$), 134.0 (C$^{1'}$), 133.4 (C$^{10c}$), 133.0 (C$^{2''}$, C$^{6''}$), 132.6 (C$^{2'}$, C$^{6'}$), 131.3 (C$^{9}$), 131.0 (C$^{2}$), 129.6 (C$^{5}$), 128.3 (C$^{3a}$), 127.0 (C$^{4}$), 123.5 (C$^{7}$), 122.1 (C$^{6}$), 121.2 (C$^{10}$), 119.3 (C$^{1}$), 115.7 (C$^{3''}$, C$^{5''}$), and 115.5 (C$^{3'}$, C$^{5'}$). $^{19}$F-NMR δ(CDCl$_3$, ppm)—−104.74 and −105.78.

**Acyl rearrangements of acetylfluoranthenes, diacetylfluoranthenes, benzoylfluoranthenes, dibenzoylfluoranthenes, fluorobenoylfluoranthene, and bis(fluorobenzoyl)fluoranthene.** In a 150-ml round-bottomed flask equipped with a magnetic stirrer and argon gas. PPA (40 g) was heated with stirring for a few minutes at a desired temperature; 0.3 g of acylfluoranthene, diacylfluoranthene, or bis(fluorobenzoyl)fluoranthene was then added. The reaction mixture was stirred for an appropriate time. It was then poured into ice and H$_2$O and stirred overnight in order to hydrolyze the complex and PPA and to facilitate the extraction of the organic compounds. The reaction product was extracted with CH$_2$Cl$_2$, washed with saturated aqueous NaHCO$_3$ and H$_2$O, dried over MgSO$_4$, filtered, and the organic solvent was evaporated in vacuum to give the crude products. These were detected and identified according to their selected $^{1}$H-NMR chemical shifts.

**Acyl rearrangement of 3,9-Ac$_2$FT.** The reaction was carried out in a 150-ml round-bottomed flask with a magnetic stirrer and anhydrous argon atmosphere, protected from moisture. PPA (133 g) was added. After stirring for few minutes at 120 °C, 3,9-Ac$_2$FT (1.0 g, 3.4 mmol) was added. The reaction mixture was stirred at 120 °C for 2 h, and then was poured into a mixture of ice and water and stirred overnight. The products were extracted with CH$_2$Cl$_2$, the organic fraction were washed with saturated NaHCO$_3$ and water, and dried over MgSO$_4$. The organic solvent was evaporated in vacuum to give a mixture that consisted of 3,9-Ac$_2$FT, 8-AcFT, and FT in the ratios 59:16:25 and 3-methylbenzo[*c,d*]fluoranthene (3-MeBcdFT). The crude product (0.7 g) was purified by column chromatography on silica gel using PE/EtOAc as eluent, starting with 98:2 and then 20:80 ratio, to give 0.1 g of 3-MeB*cd*FT as pure red powder, in 11% yield, mp. 209–210 °C; TLC $R_f$ = 0.48; MS: *m/z* = 269 (M$^{+1}$); IR: $\nu$ = 1641 cm$^{-1}$ (C=O); UV/vis (nm): $\lambda$ = 432, 414, 387 sh, 348 sh, 307 sh, 295 sh, and 247.

$^{1}$H-NMR δ(CDCl$_3$, ppm)—8.32 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{11}$), 7.80 (d, $^{3}J$ = 7.0 Hz, 1H, H$^{10}$), 7.71–7.67 (m, 2H, H$^{6}$, H$^{9}$), 7.66 (s, 2H, H$^{4}$, H$^{5}$), 7.29–7.27 (m, 2H, H$^{7}$, H$^{8}$), 6.34 (2, $^{4}J$ = 1 Hz,1H, H$^{2}$), and 2.42 (d, $^{3}J$ = 1.5 Hz, 3H, CH$_3$). $^{13}$C-NMR δ(CDCl$_3$, ppm)—185.1 (C=O), 148.9 (C$^{3a}$), 143.4 (C$^{9b}$), 140.6 (C$^{5b}$), 140.3 (C$^{5a}$), 140.2 (C$^{9a}$), 133.0 (C$^{9c}$), 130.7 (C$^{11}$), 130.4 (C$^{11a}$), 129.3 (C$^{2}$), 129.1 (C$^{7}$), 129.0 (C$^{8}$), 128.9 (C$^{3}$), 128.6 (C$^{4}$, C$^{5}$), 126.7 (C$^{11b}$), 123.0 (C$^{9}$), 122.8 (C$^{6}$), 120.6 (C$^{4}$, C$^{5}$), 120.5 (C$^{10}$), and 22.9 (CH$_3$).

**Acyl rearrangement of 8-acetyl fluoranthene** The reaction was carried out in a 150-ml round-bottomed flask with a magnetic stirrer and anhydrous argon atmosphere, protected from moisture. PPA (133 g) was added. After stirring for few minutes at 120 °C, 8-AcFT (1.0 g, 3.4 mmol) was added. The reaction mixture was stirred at 120 °C for 2 h, and then was poured into a mixture of ice and water and stirred overnight. The products were extracted with CH$_2$Cl$_2$, the organic fraction were washed with saturated NaHCO$_3$ and water, and dried over MgSO$_4$. The organic solvent was evaporated in vacuum to give a mixture of both 3-AcFT and 8-AcFT. Two new compounds were formed at reaction temperatures higher than 120 °C. Separation of the compound I was performed by PLC on silica gel, using PE/EtOAc as eluent.

**Compound I** $^{1}$H-NMR (δCDCl$_3$, ppm)—8.47 (s, H$^{7}$), 8.08 (d, $J$ = 6.5 Hz, H$^{6}$), 8.05 (d, $J$ = 8.0 Hz, H$^{10}$), 8.03 (d, $J$ = 7.0 Hz, H$^{1}$), 7.95 (d, $J$ = 6.5 Hz, H$^{3}$), 7.94 (d, $J$ = 7.5 Hz, H$^{9}$), 7.91 (d, $J$ = 8.5 Hz, H$^{4}$), 7.72 (t, $J$ = 7.5 Hz, 7.5 Hz, H$^{2}$), and 7.69 (t, $J$ = 8.0 Hz, 8.5 Hz, H$^{5}$). $^{13}$C-NMR (δCDCl$_3$, ppm)—δ = 196.7 (C=O), 143.1 (C$^{10b}$), 139.5 (C$^{7a}$), 137.2 (C$^{8}$), 136.1 (C$^{7}$), 135.9 (C$^{10a}$), 133.2 (C$^{6}$), 130.1 (C$^{3}$), 130.1 (C$^{4}$), 128.3 (C$^{5}$), 128.2 (C$^{2}$), 127.9 (C$^{9}$), 127.3 (C$^{4}$), 123.2 (C$^{7}$), 121.4 (C$^{1}$), 121.1 (C$^{10}$), and 121.0 (C$^{6}$). LC-MS: *m/z* = 633 and 431 (M$^{+1}$).

**Acyl rearrangements of fluorobenzoylfluoranthenes and 3,9-bis(fluorobenzoyl)fluoranthene (general procedure).** In a 150-ml round-bottomed flask equipped with a magnetic stirrer and argon and protected from the moisture, PPA (40 g) was heated with stirring for few minutes at a desired temperature. Selected fluorobenzoylfluoranthene or 3,9-bis(fluorobenzoyl)fluoranthene (0.3 g) was added. The reaction mixture was stirred for an appropriate time. It was then poured into ice and H$_2$O and stirred overnight in order to hydrolyze the PPA and to facilitate the extraction of the organic compounds. The reaction products were extracted with CH$_2$Cl$_2$, washed with saturated aqueous NaHCO$_3$ and H$_2$O, dried over MgSO$_4$, filtered, and the organic solvent was evaporated in vacuum to give the crude products. These were detected and identified according to their selected $^1$H-NMR chemical shifts. Column chromatography using appropriate solvent was used to separate the resulted products of the rearrangements.

## Results and discussion

Fluoranthene (FT) is a non-alternant polycyclic aromatic hydrocarbon (PAH) with $C_{2v}$ symmetry, in which a naphthalene ring and a benzene ring are fused together to give a *peri*-condensed $C_6C_6C_6C_5$ ring system. The Kekulé structures in fluoranthenes have been systematically analyzed [35]. Fluoranthenes possessing Kekulé structures were classified into three types, depending on the nature of the two C–C bonds connecting benzene and naphthalene fragments. Fluoranthene has five non-equivalent sites for mono substitution: 1, 2, and 3 at the naphthalene ring and 7 and 8 at the benzene ring. Electrophilic aromatic substitution has been shown to take place at the naphthalene ring at position 3 (α-position), and/or at the benzene ring at position 8, farther away from the "bay" regions. Monoacylation of fluoranthene gave only 3-acylfluoranthene and 8-acylfluoranthene [31, 32]. These monoacylfluoranthenes differ in their degree of overcrowding. The acyl group at position 3 is overcrowded due to the *peri*-hydrogen ($H^4$); the acyl group at position 8 is considered non - overcrowded; it is flanked by two *ortho* hydrogens ($H^7$, $H^9$). Friedel–Crafts acylations at positions 1 and 7 do not take place due to the overcrowded bay regions. Moreover, position 2 resembles the β-position of naphthalene; it is less reactive toward electrophilic attack than position 3 (α-position). Dewar-PI MO study of electrophilic aromatic substitution in fluoranthene and it's σ-complexes correctly predicted that fluoranthene undergoes electrophilic substitution preferentially at position 3 [36].

There are 25 constitutional isomers of a diacylfluoranthene. These may be classified on the basis of the positions of the acyl substituents: (i) diacylfluoranthene in which the two acyl groups are positioned at the naphthalene ring system; (ii) diacylfluoranthene in which one acyl group is positioned at the naphthalene ring and the second acyl is positioned at the benzene ring; and (iii) diacylfluoranthene in which the two acyl groups are positioned at the benzene ring. Diacylfluoranthenes of group (ii) have been claimed to be synthesized by Friedel–Crafts diacylation of fluoranthene giving 3,8-diacylfluoranthene and/or 3,9-diacylfluoranthene [31, 34].

The present study encompasses the following mono- and diacylfluoranthenes: 3-AcFT, 8-AcFT, 3,9-$Ac_2$FT, 7,10-$Ac_2$FT, 3-BzFT, 8-BzFT, 3,9-$Bz_2$FT, 3-(4-FBz)FT, 8-(4-FBz)FT, and 3,9-$(4\text{-FBz})_2$FT (Fig. 1).

### Synthesis

Friedel–Crafts acylations of fluoranthene have previously been studied. The syntheses of 3-AcFT, 8-AcFT, 3-BzFT, 8-BzFT, 3,9-$Ac_2$FT, and 7,10-$Ac_2$FT are described in the literature [31, 32, 37–39]. The present study describes in addition the synthesis of 3,9-$Bz_2$FT, 3-(4-FBz)FT, 8-(4-FBz)FT, and 3,9-$(4\text{-FBz})_2$FT. The structures of 8-AcFT, 8-BzFT, 3-BzFT, 3-(4-FBz)FT, 3,9-$Ac_2$FT, and 7,10-$Ac_2$FT have been verified by X-ray crystallography (vide infra) [40].

3-(4-FBz)FT and 8-(4-FBz)FT were synthesized by treatment of FT with 4-fluorobenzoyl chloride and $AlCl_3$ in $CH_2Cl_2$ at 0 °C for 4 h. The constitutional isomers were separated using column chromatography to give 17% of 3-(4-FBz)FT, mp. 188–189 °C, and 22% 8-(4-FBz)FT, mp. 143–144 °C.

3,9-$Bz_2$FT and 3,9-$(4\text{-FBz})_2$FT were prepared by the reactions of 8-BzFT/8-(4-FBz)FT, benzoyl chloride/4-fluorobenzoyl chloride, and $AlCl_3$ in 1,2-dichloroethane at 80 °C for 14 h. 3,9-$Bz_2$FT and 3,9-$(4\text{-FBz})_2$FT were purified by column chromatography. 3,9-$Bz_2$FT was obtained as a yellow product, 22% yield, mp. 159–160 °C. 3,9-$(4\text{-FBz})_2$FT was obtained as a pale yellow, yield 15%, mp. 184–186 °C.

In the present study, the reaction of 8-AcFT, acetyl chloride and $AlCl_3$ in dry $CH_2Cl_2$ starting at 0 °C, then at room temperature for 1 h gave one constitutional isomer of diacetylfluoranthene, 3,9-$Ac_2$FT. mp. 139–140 °C (lit. 137–139 °C [31, 34]). The same isomer was obtained by the analogous acetylation of 3-AcFT. The previous reported studies of Friedel–Crafts acetylation of 3-AcFT and 8-AcFT, with 2.3 equivalents of acetyl chloride and $AlCl_3$ in $CH_2Cl_2$ for 4 h at room temperature gave 42% of a diacetylfluoranthene, without unequivocally determining its exact structure [31, 41]. We note that the Friedel–Crafts acetylations of 3-AcFT and 8-AcFT to give 3,9-$Ac_2$FT were regioselective.

### NMR spectroscopy

The structures of AcFTs, BzFTs and (4-FBz)FTs have been verified by $^1$H- and $^{13}$C-NMR spectra. Table 1 gives the $^1$H-NMR chemical shifts of AcFTs, BzFTs, and (4-FBz)FTs. Table 2 gives the $^1$H-NMR chemical shifts of hydrogens *peri* and *ortho* to the carbonyl, $^{13}$C-NMR chemical shifts of the carbonyl group, and $^{19}$F-NMR chemical shifts.

In 3-AcFT, 3-BzFT, and 3-(4-FBz)FT, the hydrogens located *peri* to the carbonyl group ($H^4$) are deshielded more than the hydrogens *ortho* to the carbonyl group ($H^2$). Both $H^2$ and $H^4$ were considerably deshielded as compared with the hydrogens of unsubstituted FT. The differences in the chemical shifts between the hydrogens *peri* and *ortho* to the carbonyl to those of unsubstituted FT are noted: $\Delta\delta(H^4) = 0.92$ ppm, $\Delta\delta(H^2) = 0.53$ ppm (3-AcFT), $\Delta\delta(H^4) = 0.32$ ppm, $\Delta\delta(H^2) = 0.24$ ppm (3-BzFT), and $\Delta\delta(H^4) = 0.26$ ppm, $\Delta\delta(H^2) = 0.18$ ppm (3-(4-FBz)FT). A similar deshielding effect was evident in the chemical shifts of $H^7$ which is located *ortho-* to the carbonyl group in 8-AcFT, 8-BzFT, and 8-(4-FBz)FT. The differences in chemical shift between these compounds and unsubstituted FT were 0.57, 0.49, and 0.44 ppm, respectively.

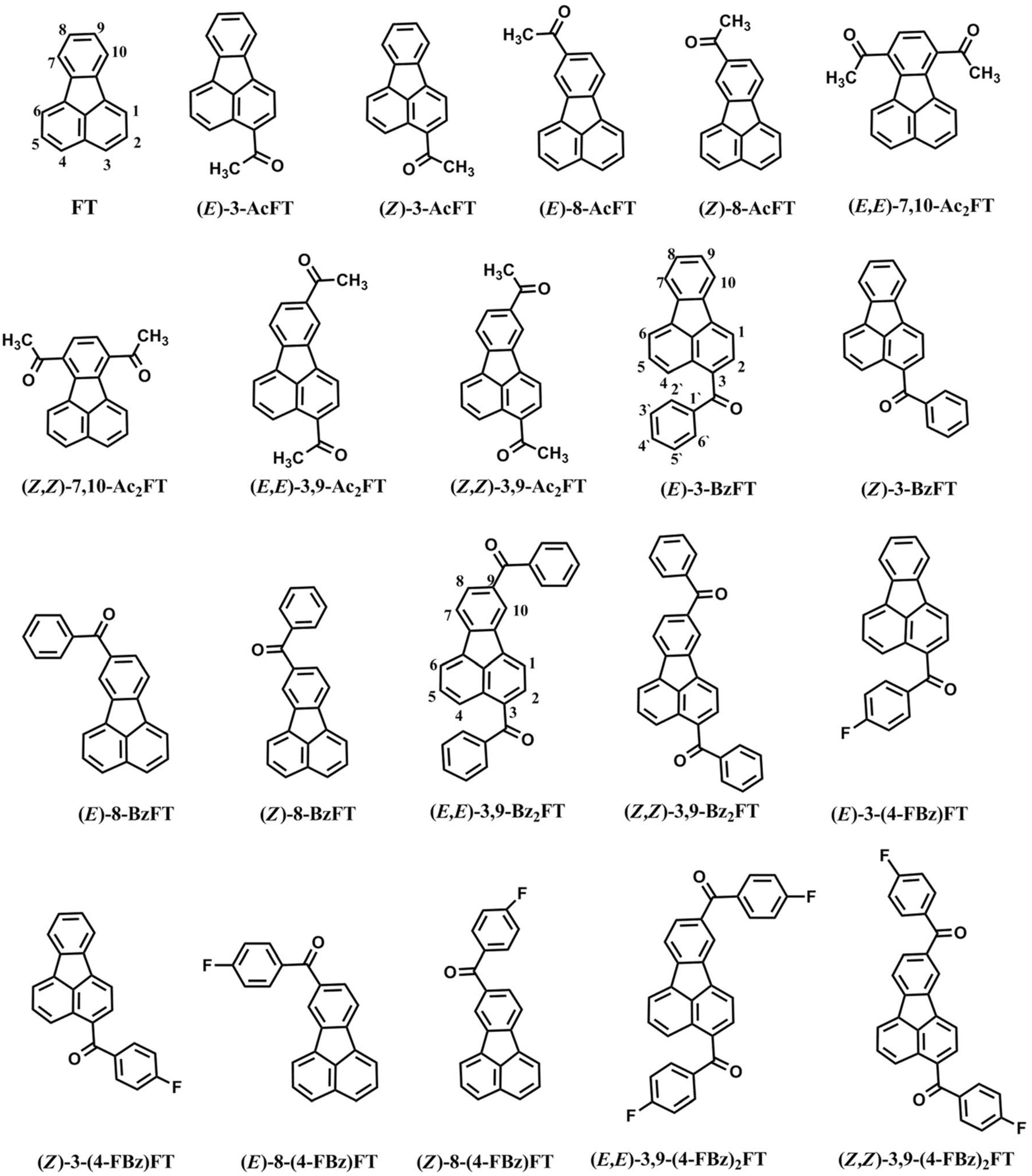


**Fig. 1** Acetyl-, diacetyl-, benzoyl-, dibenzoyl-, 4-fluorobenzoyl-, and bis(4-fluorobenzoyl)fluoranthenes under study

## Molecular and crystal structures

The crystal and molecular structures of the fluoranthene derivatives 8-AcFT, 3,9-$Ac_2$FT, 7,10-$Ac_2$FT, 3-BzFT, 8-BzFT, and 3-(4-FBz)FT were determined by X-ray crystallography [40]. Ketones 8-AcFT and 8-BzFT crystallized in the orthorhombic space group *Pbca* with $C_1$ symmetry. Ketones 3,9-$Ac_2$FT, 3-BzFT, and 3-(4-FBz)FT crystallized in the monoclinic space groups $P2_1/c$, $P2_1/n$, and $P2_1/n$, respectively with $C_1$ symmetry. Ketone 7,10-$Ac_2$FT crystallized in the orthorhombic space group $P2_12_12_1$ with $C_2$ symmetry. The ORTEP diagrams of their molecular structures are presented in Figs. 2 and 3. Table 3 gives their crystallographic data. Table 4 gives selected geometrical parameters derived from the X-ray crystal structures of 8-AcFT, 3,9-$Ac_2$FT, 3-BzFT, 8-BzFT, and 3-(4-FBz)FT under study.

A characteristic geometric parameter of acylfluoranthene species is the torsion angle ($\tau$) of the acyl group relative to the fluoranthene system: $C^{3a}$–$C^3$–$C^{11}$–$O^{12}$ for 3-BzFT and 3-(4-FBz)FT, $C^7$–$C^8$–$C^{11}$–$O^{12}$ for 8-AcFT and 8-BzFT, $C^{3a}$–$C^3$–$C^{11}$–$O^{12}$ and $C^{10}$–$C^9$–$C^{11}$–$O^{12}$ for 3,9-$Ac_2$FT, and $C^{6b}$–$C^7$–$C^{11'}$–$O^{12'}$ and $C^{10a}$–$C^{10}$–$C^{11}$–$O^{12}$ for 7,10-$Ac_2$FT. For benzoylfluoranthenes, there is also the torsion angle ($\upsilon$) of

**Table 1** $^{1}$H-NMR chemical shifts (δ, ppm) of mono- and diacylfluoranthenes in $CDCl_3$

| | $H^1$ | $H^2$ | $H^3$ | $H^4$ | $H^5$ | $H^6$ | $H^7$ | $H^8$ | $H^9$ | $H^{10}$ | $CH_3$ | $H^{2'}$, $H^{2''}$ | $H^{3'}$, $H^{3''}$ | $H^{4'}$, $H^{4''}$ | $H^{5'}$, $H^{5''}$ | $H^6$, $H^{6''}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FT | 7.95 d | 7.64 t | 7.85 d | 7.85 d | 7.64 t | 7.95 d | 7.92 dd | 7.42–7.39 m | 7.42–7.39 m | 7.92 dd | – | – | – | – | – | – |
| 3-AcFT | 7.91 d | 8.17 d | – | 8.77 d | 7.68 td | 7.89–7.88 m | 7.86 dd | 7.43 td | 7.35 td | 7.89–7.88 m | 2.79 s | – | – | – | – | – |
| 8-AcFT | 8.02 d | 7.68 t | 7.92 d | 7.89 d | 7.68 t | 8.02 d | 8.49 s | – | 7.99 dd | 7.95 d | 2.71 s | – | – | – | – | – |
| 3,9-$Ac_2$FT | 8.00 d | 8.22 d | – | 8.86 dd | 7.74 dd | 7.98 dd | 7.92 dd | 8.03 dd | – | 8.48 s | 2.80 s<br>2.71 s | – | – | – | – | – |
| 7,10-$Ac_2$FT | 8.33 d | 7.64 d | 7.91 d | 7.91 d | 7.64 d | 8.33 d | – | 7.58 s | 7.58 s | – | 2.78 s | – | – | – | – | – |
| 3-BzFT | 7.95 dd | 7.85 d, | – | 8.17 d | 7.66 td | 7.95 dd | 7.93–7.92 m | 7.44 td | 7.40 td | 7.93–7.92 m | – | 7.89 d | 7.45 t | 7.62 t | 7.45 t | 7.89 d |
| 8-BzFT | 8.02 d | 7.69 t | 7.92 d | 7.95 d | 7.71 t | 8.07 d | 8.40 s | – | 7.86 d | 8.01 d | – | 7.89 d | 7.54 t | 7.63 t | 7.54 t | 7.89 d |
| 3,9-$Bz_2$FT | 8.01 d | 7.91–7.87 m | – | 8.26 d | 7.72 td | 8.06 d | 8.00 d | 7.91–7.87 m | – | 8.46 s | – | 7.91–7.87 m | 7.52[a] t | 7.64 t | 7.51[b] t | 7.91–7.87 m |
| 3-(4-FBz)FT | 7.95 d | 7.82 d | – | 8.10 d | 7.65 td | 7.94 d | 7.44 td | 7.89 d | 7.89 d | 7.41 td | – | 7.93 d | 7.17 t | – | 7.93 d | 7.17 t |
| 8-(4-FBz)FT | 8.07 d | 7.71 t | 7.95 d | 7.95 d | 7.69 t | 8.02 d | 8.36 s | – | 7.82 dd | 8.01 d | – | 7.21 t | 7.92 dd | – | 7.92 dd | 7.21 t |
| 3,9-(4-$FBz)_2$FT | 8.03 d | 7.86 t | – | 8.21 dd | 7.73 td | 8.08 d | 8.02 d | 7.86 dd | – | 8.39 s | – | 7.99–7.92 m | 7.22[c] t | – | 7.19[d] t | 7.99–7.92 m |

[a] $H^{3'}$,$H^{3''}$

[b] $H^{5'}$,$H^{5''}$

[c] $H^{3'}$,$H^{5''}$

[d] $H^{3'}$,$H^{5''}$

**Table 2** $^{1}$H-, $^{13}$C-, and $^{19}$F-NMR chemical shifts (δ, ppm) of mono- and diacylfluoranthenes in $CDCl_3$

| | *Peri*-H | *Ortho*-H | | | $^{19}$F-NMR | $^{13}$C-NMR |
|---|---|---|---|---|---|---|
| 3-AcFT | 8.77 ($H^4$) | 8.17 ($H^2$) | – | – | – | 200.4 |
| 8-AcFT | – | 8.49 ($H^7$) | 7.99 ($H^9$) | – | – | 197.9 |
| 3,9-$Ac_2$FT | 8.86 ($H^4$) | 8.22 ($H^2$) | 8.48 ($H^{10}$) | 8.03 ($H^8$) | – | 200.3, 197.6 |
| 7,10-$Ac_2$FT | – | 7.58 ($H^8$) | 7.58 ($H^9$) | – | – | 202.13 |
| 3-BzFT | 8.17 ($H^4$) | 7.85 ($H^2$) | – | – | – | 197.2 |
| 8-BzFT | – | 8.41 ($H^7$) | 7.86 ($H^9$) | | – | 196.7 |
| 3,9-$Bz_2$FT | 8.26 ($H^4$) | 7.89 ($H^2$) | 7.89 ($H^8$) | 8.46 ($H^{10}$) | – | 196.9, 196.5 |
| 3-(4-FBz)FT | 8.10 ($H^4$) | 7.82 ($H^2$) | – | – | −105.26 | 195.5 |
| 8-(4-FBz)FT | – | 8.36 ($H^7$) | 7.82 ($H^9$) | – | −106.25 | 195.3 |
| 3,9-(4-FBz)$_2$FT | 8.21 ($H^4$) | 7.86 ($H^2$) | 8.39 ($H^{10}$) | 7.86($H^8$) | −104.73, −105.78 | 195.2, 194.9 |

the acyl group relative to the benzene ring $C^{2'}$–$C^{1'}$–$C^{11}$–$O^{12}$. In addition, the dihedral angle ($\theta$) between the planes of the fluoranthene and benzene aromatic systems was defined. Conformations of the acyl groups are denoted as *E* when $\tau$ is greater than 90° or as *Z* when $\tau$ is less than 90°.

The carbonyl group in 3-BzFT is tilted out of the planes of the fluoranthene ring system and the phenyl ring by $\tau = 28°$ and 27°, respectively, with a dihedral angle $\theta = 58°$. 3-BzFT is a slightly overcrowded isomer; its $O^{12\cdots}H^4$ contact distance is 239 pm, slightly shorter than the sum of the respective Van-der-Waals radii of hydrogen (115 pm) and oxygen (129 pm) [42].

8-AcFT is considered an essentially planar PAKs with $\tau = 2°$ and $\theta = 4°$. The carbonyl group in 8-BzFT, unlike that in 8-AcFT is twisted out of the planes of fluoranthene and phenyl moieties by $\tau = 23°$ and $\upsilon = 32°$ with a large dihedral angle $\theta = 52°$.

3,9-$Ac_2$FT has a large torsion angle of the carbonyl group at position 3 ($\tau_3 = 22°$) and a small torsion angle of the carbonyl group at position 9 ($\tau_9 = 3°$). In 7,10-$Ac_2$FT, $\tau_7 = 33°$, and $\tau_{10} = 32°$, the dihedral angles between the acetyl plane and fluoranthene plane are relatively large: $\theta_7 = 37°$ and $\theta_{10} = 38°$. This large titling of the carbonyl groups out of the fluoranthene plane is mostly due to the bay regions.

None of the PAKs under study adopts a fully planar conformation in their crystal structures. All acylfluoranthenes crystallize as *Z* or *Z,Z*-diastereomers with $C_1$ symmetry. The values of their carbonyl torsion angles vary. Mono- and diacylfluoranthenes under study are arranged in the following order of decreasing torsion angles $\tau$:

$$7{,}10\text{−}Ac_2FT > 3\text{−}BzFT > 3\text{−}(4\text{−}FBz)FT > 8\text{−}BzFT$$
$$> 3{,}9\text{−}Ac_2FT > 8\text{−}AcFT$$

## Friedel–Crafts acyl rearrangements

The Friedel–Crafts acyl rearrangements of AcFTs, $Ac_2$FTs, BzFTs, 3,9-$Bz_2$FT, (4-FBz)FTs, and 3,9-(4-FBz)$_2$FT in PPA were studied at various temperatures and for various periods of time using PPA as a solvent. The compounds were subjected to PPA at 80–160 °C for 2–6 h. The results of the rearrangements were characterized by the low-field $^{1}$H-NMR chemical shifts of the hydrogens *ortho* and *peri* to carbonyl group. The results of the acyl rearrangements of AcFTs versus BzFTs and $Ac_2$FT versus $Bz_2$FT are given in Table 5. Other rearranged products are excluded. Scheme 1 describes the Friedel–Crafts acyl rearrangements of AcFTs and 3,9-$Ac_2$FT.

**3-AcFT** Friedel–Crafts acyl rearrangements of 3-AcFT in PPA gave both 3-AcFT and 8-AcFT. The ratio of 8-AcFT increased considerably by lengthening the time and raising the temperature of the reaction. FT was also formed upon prolonging the time of the reaction and raising the temperature.

**8-AcFT** The reaction of 8-AcFT in PPA at temperatures below 100 °C for varying reaction times did not indicate any acyl rearrangements or deacetylation. At higher temperatures, 8-AcFT, in contrast to 3-AcFT, underwent only deacetylation to give FT. However, during the reactions of both 3-AcFT and 8-AcFT at temperatures higher than 120 °C, two new rearrangement products were formed. The first compound I was separated by PLC, using PE/EtOAc as eluent. Compound I was tentatively characterized by its $^{1}$H- and $^{13}$C-NMR spectra. The singlet at δ = 8.47 ppm assigned to $H^7$ is noted. Also, the signal at $m/z = 431$ in the mass spectrum of I is attributed to an $(8\text{-FT})_2C{=}O^{+1}$ ($C_{33}H_{18}O^{+1}$) species. The structure of the second compound (traces) was not elucidated. A possible pathway of the formation of bis (8-fluoranthenyl) ketone ($(8\text{-FT})_2C{=}O$) is oxidation and deacetylation of 8-AcFT to give 8-fluoranthene carboxylic acid (8-$FTCO_2H$) and FT, respectively, followed by Friedel–Crafts acylaion of FT by 8-$FTCO_2H$.

**3,9-$Ac_2$FT** The major rearrangement product of the reactions of 3,9-$Ac_2$FT in PPA at high temperatures was 3-methyl-1*H*-benzo[*cd*]fluoranthen-1-one (3-MeB*cd*FT); 8-AcFT was also

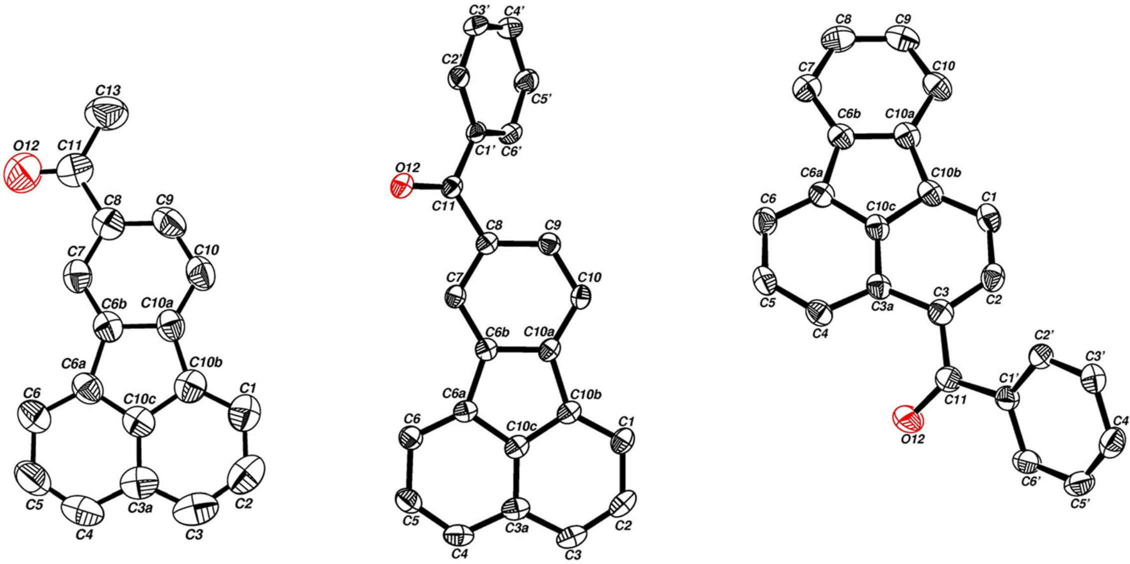


**Fig. 2** ORTEP drawings of the X-ray molecular structures of (*Z*)-8-AcFT (*left*), (*Z*)-8-BzFT (*middle*), and (*Z*)-3-BzFT (*right*)

formed. The structure of the rearrangement product 3-MeB*cd*FT was determined by $^{1}$H- and $^{13}$C-NMR spectra.

The mass spectrum of the rearrangement product of 3,9-$Ac_2$FT indicated a $C_{20}H_{12}O$ species ($M^+ = 268$). The following three constitutional isomers were considered: 3-methyl-1*H*-benzo[*cd*]fluoranthen-1-one (3-MeB*cd*FT), 3-methyl-1*H*-cyclopenta[*k*]fluoranthen-1-one (3-MeCP*k*FT), and 3-methyl-1*H*-cyclopenta[*l*]fluoranthen-1-one (3-MeCP*l*FT) (Fig. 4). The choice of 3-MeB*cd*FT was based on the NOE signal between $CH_3$ (2.42 ppm) and $H^4$ (7.66 ppm). The low-field doublet at 8.32 ppm representing $H^{11}$ is unlikely to represent any other hydrogens in the other two constitutional isomers. The $^{1}$H-NMR chemical shifts of the rearrangement product are consistent with the reported chemical shifts for 1*H*–benzo[*cd*]fluoranthen-1-one (B*cd*FT) [43] (Fig. 4), e.g., the low-field doublet of $H^4$ (not $H^{11}$) at 8.28 ppm and the four proton multiplet in the range 7.2–7.7 ppm.

A possible mechanism for the formation of 3-MeB*cd*FT is described in Scheme 2: deacetylation of the 9-acetyl group of 3,9-$Ac_2$FT to give 3-AcFT and acetylium ion, acetylation of the enol of 3-AcFT, followed by intramolecular Friedel–Crafts alkylation to give 3-MeB*cd*FT.

**7,10-$Ac_2$FT** This ketone did not undergo any rearrangement or deacylation in PPA over a wide range of temperatures (60–160 °C) and for various times of the reactions. The reason for this lack of reactivity is probably the deactivation effect of the second acetyl group at position 10 toward deacylation of the acetyl group at position 7.

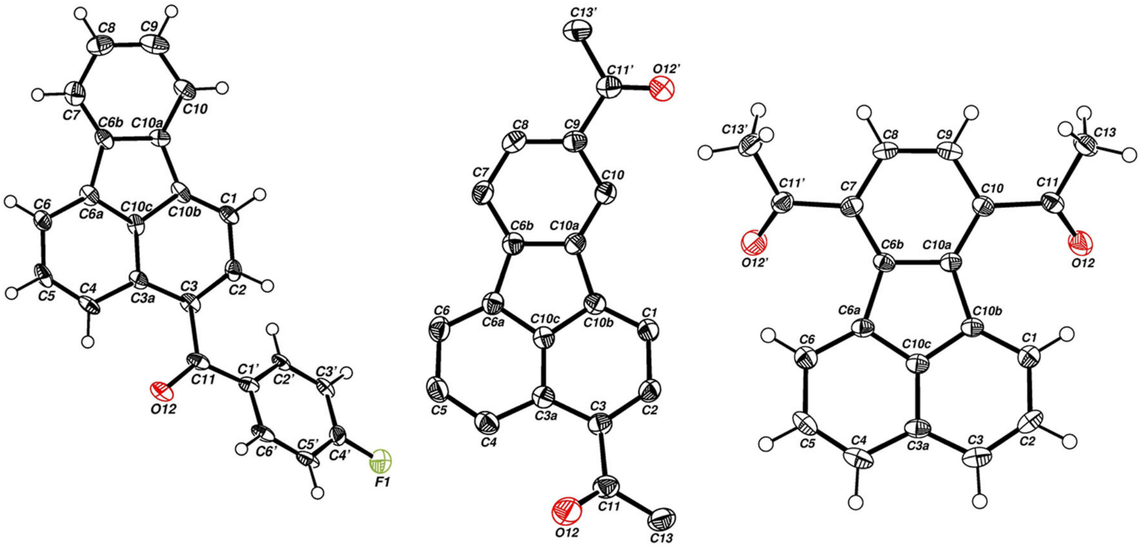


**Fig. 3** ORTEP drawings of the X-ray molecular structures of (*Z*)-3-(4-FBz)FT (*left*), (*Z,Z*)-3,9-$Ac_2$FT (*middle*), and (*Z,Z*)-7,10-$Ac_2$FT (*right*)

**Table 3** Crystallographic data for the acylfluoranthenes under study

| | 8-AcFT | 3,9-$Ac_2$FT | 3-BzFT | 8-BzFT | 3-(4-FBz)FT | 7,10-$Ac_2$FT |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{18}H_{12}O$ | $C_{20}H_{14}O_2$ | $C_{23}H_{14}O$ | $C_{23}H_{14}O$ | $C_{23}H_{13}FO$ | $C_{20}H_{14}O_2$ |
| Temperature (K) | 295 (1) | 173 (1) | 173 (1) | 173 (1) | 173 (1) | 173 (1) |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | Pbca | $P2_1/c$ | $P2_1/n$ | Pbca | $P2_1/n$ | $P2_12_12_1$ |
| *a* (°A) | 13.833 (2) | 11.9313 (6) | 4.0946 (2) | 7.3362 (5) | 4.0169 (8) | 7.5756 (5) |
| *b* (°A) | 7.754 (1) | 7.2530 (4) | 29.687 (2) | 18.313 (1) | 31.132 (6) | 9.4417 (6) |
| *c* (°A) | 23.805 (4) | 17.1787 (8) | 12.3288 (7) | 22.493 (2) | 12.191 (3) | 19.049 (1) |
| $\alpha$ (deg) | 90° | 90° | 90°. | 90° | 90° | 90° |
| $\beta$ (deg) | 90° | 107.056(1)° | 94.236(1)° | 90° | 94.410(4)° | 90° |
| $\gamma$ (deg) | 90° | 90° | 90°. | 90° | 90° | 90° |
| Volume (°$A^3$) | 2553.6(7) | 1421.2(1) | 1494.6(1) | 3021.8(3) | 1520.0(5) | 1362.5(2) |
| *Z* | 8 | 4 | 4 | 8 | 4 | 4 |
| Density (calc.; $Mg/m^3$) | 1.271 | 1.338 | 1.361 | 1.347 | 1.417 | 1.396 |
| Reflections collected | 25,808 | 15,721 | 17,101 | 31,211 | 10,911 | 15,856 |
| Independent Reflections | 2775 ($R_{int}$ = 0.0487) | 3407 ($R_{int}$ = 0.0193) | 3560 ($R_{int}$ = 0.0231) | 3301 ($R_{int}$ = 0.0293) | 3290 ($R_{int}$ = 0.0763) | 3240 ($R_{int}$ = 0.0284) |
| Final *R* indices ($I > 2\sigma_I$) | $R_1$ = 0.1010, w$R_2$ = 0.2024 | $R_1$ = 0.0495, w$R_2$ = 0.1290 | $R_1$ = 0.0597, w$R_2$ = 0.1347 | $R_1$ = 0.0494, w$R_2$ = 0.1172 | $R_1$ = 0.1478, w$R_2$ = 0.2912 | $R_1$ = 0.0483, w$R_2$ = 0.1158 |

**3-BzFT** The reaction of 3-BzFT in PPA was carried out at different times and temperatures of the reaction. The rearrangement of 3-BzFT started at low temperature, e.g., at 80 °C for 2 h to give 8-BzFT. At 100 °C for 2 h, the reaction gave 8-BzFT and 3,9-$Bz_2$FT in the ratio 26:3. This ratio increased by lengthening the time and raising the reactions temperature. At 160 °C for 4 h, the results indicated almost complete debenzoylation of 3-BzFT to FT and rearrangement to 8-BzFT; the ratio was 1 (3-BzFT): (8-BzFT): 90 (FT).

**8-BzFT** The reaction of 8-BzFT in PPA at 60–100 °C for 2–6 h did not give any 3-BzFT. Debenzoylation to FT was observed at temperatures higher than 120 °C. At 160 °C, almost complete debenzoylation to FT occurred; the ratio 8-BzFT: FT at 160 °C for 6 h was 7:93.

**3,9-$Bz_2$FT** The reaction of 3,9-$Bz_2$FT in PPA was also studied. Debenzoylation started at high temperature (140 °C for 4 h) to give 8-BzFT in the ratio 72 (3,9-BzFT): 28 (8-BzFT). Upon prolonging the reaction time, e.g., 140 °C for 6 h, debenzoylation to FT also took place. In the acyl rearrangement experiments of 3,9-$Bz_2$FT, there was no indication for the formation of rearrangement products, in contrast to 3,9-$Ac_2$FT. An aldol condensation is not possible in this case.

The results of Friedel–Crafts acyl rearrangements of 3-BzFT and 8-BzFT correspond well with the degree of deviation from planarity of the carbonyl group(s). The data given in Table 5 indicate that 8-BzFT with a relatively small torsion angle as compared with 3-BzFT, underwent deacylation and acyl rearrangements more difficultly than 3-BzFT.

The introduction of a fluorine atom at the *para* positions of the phenyl group hardly affected the results of rearrangements. (4-FBz)FTs acted in the same way as BzFTs. The only differences were the ratios and the temperatures at which the rearrangements started.

**3-(4-FBz)FT** Friedel–Crafts acyl rearrangements of 3-(4-FBz)FT started at 80 °C to give 8-(4-FBz)FT. At higher temperature, 120 °C for 2 h, 3-(4-FBz)FT, 8-(4-FBz)FT, 3,9-(4-FBz)$_2$FT, and FT were formed in the ratios of 41:42:5:12, respectively. The relative amount of FT increased upon raising the temperature. At 140 °C for 6 h, 100% of FT was formed.

**8-(4-FBz)FT** The reaction of 8-(4-FBz)FT in PPA at temperatures below 100 °C gave only the starting ketone. At temperatures above 120 °C, the deacylation product FT started to appear. The relative amount of FT increased upon raising the temperature and prolonging the time of the reactions. At 140 °C for 2 h, 3,9-(4-FBz)$_2$FT was formed; the ratios were 83 (8-(4-FBz)FT):2 (3,9-(4-FBz)$_2$FT):15 (FT). At 160 °C for 6 h, the ratio of 8-(4-FBz)FT to FT was 13:87, whereas 3,9-(4-FBz)$_2$FT were not formed. The only difference in behavior between 8-(4-FBz)FT and 8-BzFT was the formation of 3,9-(4-FBz)$_2$FT from the former at temperatures higher than 120 °C. Table 6 summarizes the Friedel–Crafts acyl

**Table 4** Selected geometrical parameters of 3-BzFT, 8-AcFT, 8-BzFT, 3-(4-FBz)FT, 3,9-$Ac_2FT$, and 7,10-$Ac_2FT$ derived from their X-ray crystal structures

| | $\theta$ (deg) | $\tau$ (deg) | $\upsilon$ (deg) | $C_{carb}$–$C_{arom}$[a] (pm) | O···H (pm) | $CH_3$···H/H···H (pm) |
|---|---|---|---|---|---|---|
| (*Z*)-3-BzFT | | | | | | |
| $C_1$ | 57.6 | 27.7<br>−146.4 | 27.4<br>−149.0 | 149.1<br>149.7 | 239.8, $H^4$<br>253.4, $H^{6'}$ | 240.3, $H^{2}\cdots H^{2'}$ |
| (*Z*)-8-AcFT | | | | | | |
| $C_1$ | 4.7 | −1.9<br>176.8 | – | 149.9 | 249.6, $H^7$ | 262.2, $C^{13}\cdots H^9$ |
| (*Z*)-8-BzFT | | | | | | |
| $C_1$ | 52.4 | 22.7<br>−154.7 | 31.87<br>−142.3 | 149.2<br>149.8 | 252.0, $H^7$<br>257.9, $H^{2'}$ | 246.6, $H^{9}\cdots H^{6'}$ |
| (*Z*)-3-(4-FBz)FT | | | | | | |
| $C_1$ | 55.85 | −23.54 | −30.14 | 149.2 | 238.7, $H^4$ | 235.0, $H^{2}\cdots H^{2'}$ |
| | | 150.73 | 146.9 | 148.8 | 251.9, $H^{6'}$ | |
| (*Z*,*Z*)-3,9-$Ac_2FT$ | | | | | | |
| $C_1$ | 5.26 | 2.7<br>−178.3 | – | 149.5 | 234.7, $H^4$ | 259.2, $C^{13}\cdots H^2$ |
| | 24.7 | −21.7<br>155.15 | – | 149.5 | 247.5, $H^{10}$ | 261.7, $C^{13'}\cdots H^8$ |
| (*Z*,*Z*)-7,10-$Ac_2FT$ | | | | | | |
| $C_2$ | 37.2 | −33.38<br>144.4 | – | 150.5 | 227.3, $H^6$ | 260.9, $C^{13}\cdots H^9$ |
| | 38.31 | 32.34<br>−143.18 | – | 150.2 | 230.0, $H^1$ | 260.3, $C^{13'}\cdots H^8$ |

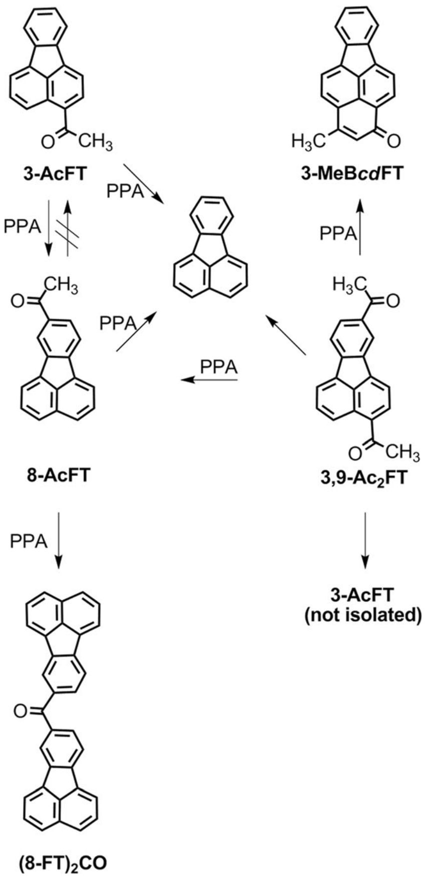
[a] $C^3$–$C^{11}$ and $C^{1'}$–$C^{11}$ for 3-BzFT, $C^8$–$C^{11}$ for 8-AcFT, $C^8$–$C^{11}$ and $C^1$–$C^{11}$ for 8-BzFT, $C^3$–$C^{11}$ and $C^{1'}$–$C^{11}$ for 3-BzFT, $C^3$–$C^{11}$ and $C^9$–$C^{11}$ for 3,9-$Ac_2FT$, and $C^7$–$C^{11}$ and $C^{10}$–$C^{11'}$ for 7,10-$Ac_2FT$

rearrangements of BzFTs and $Bz_2FT$ as compared to 4-FBzFTs and 4-$(FBz)_2FT$.

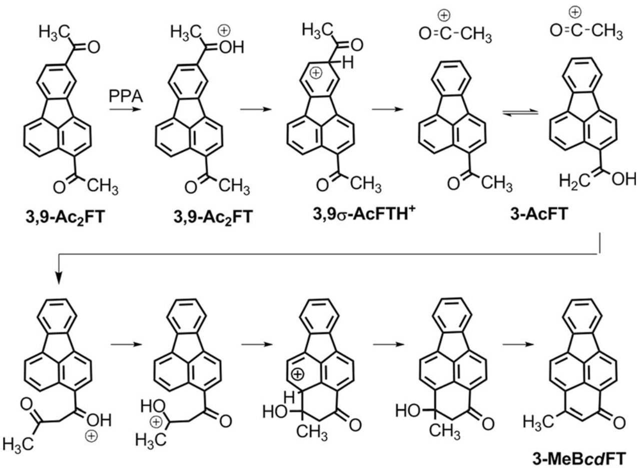
**3,9-(4-FBz)$_2$FT** No rearrangements were observed when 3,9-$(4\text{-}FBz)_2FT$ was treated with PPA at temperatures lower than 120 °C, 4 h. Upon prolonging the time of the reactions, 8-(4-FBz)FT started to form and its relative amount increased upon prolonging the time and increasing the temperature. At 140 °C for 4 h the ratios were 53 (3,9-$(4\text{-}FBz)_2FT$):17 (8-(4-FBz)FT):30 (FT). Treatment of 3,9-$(4\text{-}FBz)_2FT$ with PPA at 120 °C for 6 h gave only (3,9-$(4\text{-}FBz)_2FT$) and (8-(4-FBz)FT) in the ratio 96:4, respectively. At

**Table 5** Products of Friedel–Crafts acyl rearrangements of AcFTs, BzFTs, $Ac_2FTs$, and $Bz_2FTs$

| Starting material | Temperature (°C) | Time (h) | 3-XFT | | 8-XFT | | 3,9-$X_2FT$ | | FT |
|---|---|---|---|---|---|---|---|---|---|
| | | | *X* = Ac | *X* = Bz | *X* = Ac | *X* = Bz | *X* = Ac | *X* = Bz | |
| 3-AcFT | 80 | 6 | 95 | – | 5 | – | – | – | 0 |
| 3-AcFT | 120 | 2 | 15 | – | 36 | – | – | – | 43 |
| 3-BzFT | 100 | 2 | – | 71 | – | 26 | – | 3 | 0 |
| 3-BzFT | 160 | 4 | – | 1 | – | 9 | – | 0 | 90 |
| 8-AcFT | 100 | 2 | – | – | 100 | – | – | – | – |
| 8-AcFT | 160 | 6 | – | – | 17 | – | – | – | 78 |
| 8-BzFT | 100 | 2 | – | – | – | 100 | – | – | – |
| 8-BzFT | 160 | 6 | – | – | – | 7 | – | – | 93 |
| 3,9-$Ac_2FT$ | 80 | 6 | – | – | 0 | – | 100 | – | – |
| 3,9-$Ac_2FT$ | 100 | 6 | – | – | 13 | – | 66 | – | – |
| 3,9-$Bz_2FT$ | 100 | 6 | – | – | – | – | – | 100 | – |
| 3,9-$Bz_2FT$ | 140 | 4 | – | – | – | 28 | – | 72 | – |
| 3,9-$Bz_2FT$ | 140 | 6 | – | – | – | 33 | – | 21 | 46 |



**Scheme 1.** Friedel–Crafts acyl rearrangements of AcFTs and 3,9-Ac$_2$FT



**Scheme 2** Possible pathway of formation of 3-MeB*cd*FT

140 °C for 6 h, the reaction gave 3,9-(4-FBz)$_2$FT and 8-(4-FBz)FT in the ratio 41:59, respectively.

## DFT study

3- and 8-Acetylfluoranthenes (3-AcFT and 8-AcFT), 3,8- and 3,9-diacetylfluoranthenes (3,8-Ac$_2$FT and 3,9-Ac$_2$FT), and their derivatives which may be involved in their Friedel–Crafts acyl rearrangements, were subjected to a systematic DFT study. Calculations at B3LYP/6-31G(*d*) were carried out for the species in the gas phase and in formic acid environment, by placing the solute in a cavity within the solvent ($HCO_2H$) reaction field, using the polarizable continuum model (PCM) [30]. Recently, a computational model for predicting the site for electrophilic aromatic substitution was reported [44, 45]. The model was based on DFT calculations of the relative stabilities of σ-complex intermediate and applied (inter alia) to Lewis-acid-promoted Friedel–Crafts acylations. AcFTs may adopt (each) two diastereomeric conformers *E* and *Z*; both of them were considered for non-charged species; in addition, the methyl group may adopt an *eclipsed* or a *staggered* conformation. *O*-protonates may adopt *anti*- and *syn*-orientations of the hydroxyl proton. Full conformational search was performed to find the conformations of σ-complexes arising due to the free rotation around the $sp^3$ $C^3$–$C^{11}$/$C^8$–$C^{11}$ bonds. The results of the DFT calculations of the acetylfluoranthenes (AcFTs), their corresponding *O*-protonates and σ-complexes in formic acid environment are presented in Tables 7 and 8 (only the global minima conformations are shown; see Electronic supplementary material for the complete data).

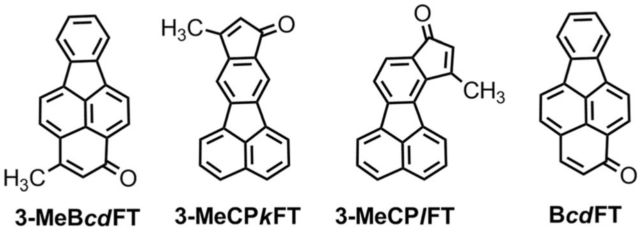


**Fig. 4** Polycyclic aromatic ketones related to the acyl rearrangement of 3,9-Ac$_2$FT

According to the results of the DFT calculations, acetylfluoranthenes 3-AcFT, 8-AcFT, and *O*-protonate 3-AcFTH$^+$ adopt the *Z* conformations as their global minima. 8-AcFT adopts the *Z* conformation also in the X-rays structure (vide supra). The global minimum (*E*)-8-AcFTH$^+$ is only 1.2 kJ/mol higher in energy than its *Z*-diastereomer. In the series of diacetylfluoranthenes, (*Z*,*E*)-3,8-Ac$_2$FT and (*Z*,*Z*)-3,9-Ac$_2$FTH$^+$ are the global minima conformations, with (*Z*,*Z*)-3,8-Ac$_2$FTH$^+$ only 0.4 kJ/mol higher in energy than (*Z*,*E*)-3,8-Ac$_2$FT. The gas phase calculations gave *Z*-diastereomers of 8-AcFTH$^+$ and (*Z*,*Z*)-3,8-Ac$_2$FTH$^+$ as the respective global

**Table 6** Products of Friedel–Crafts acyl rearrangements of BzFTs, $Bz_2FT$, 4-FBzFTs, and $4\text{-}(FBz)_2FT$

| Starting material | Temperature (°C) | Time (h) | 3-*X*FT | | 8-*X*FT | | 3,9-$X_2$FT | | FT |
|---|---|---|---|---|---|---|---|---|---|
| | | | *X* = Bz | *X* = 4-FBz | *X* = Bz | *X* = 4-FBz | *X* = Bz | *X* = 4-FBz | |
| 3-BzFT | 100 | 2 | 71 | – | 26 | – | 3 | – | 0 |
| 3-BzFT | 160 | 4 | 1 | – | 9 | – | 0 | – | 90 |
| 3-(4-FBz)FT | 80 | 4 | – | 100 | – | 0 | – | 0 | – |
| 3-(4-FBz)FT | 120 | 2 | – | 41 | – | 42 | – | 5 | 12 |
| 3-(4-FBz)FT | 140 | 4 | – | 30 | – | 15 | – | 0 | 54 |
| 8-BzFT | 100 | 2 | 0 | – | 100 | – | 0 | – | – |
| 8-BzFT | 160 | 6 | 0 | – | 7 | – | 0 | – | 93 |
| 8-(4-FBz)FT | 80 | 4 | – | 0 | – | 100 | – | 0 | – |
| 8-(4-FBz)FT | 140 | 2 | – | 0 | – | 83 | – | 2 | 15 |
| 8-(4-FBz)FT | 140 | 6 | – | 0 | – | 36 | – | 2 | 62 |
| 8-(4-FBz)FT | 160 | 6 | – | 0 | – | 13 | – | 0 | 87 |
| 3,9-$Bz_2$FT | 100 | 6 | 0 | – | 0 | – | 100 | – | – |
| 3,9-$Bz_2$FT | 140 | 6 | 0 | – | 33 | – | 21 | – | 46 |
| 3,9-$(4\text{-}FBz)_2$FT | 100 | 6 | – | 0 | – | 0 | – | 100 | – |
| 3,9-$(4\text{-}FBz)_2$FT | 140 | 4 | – | 0 | – | 17 | – | 53 | 30 |

minima conformations. These results show the preference of *Z* conformations of an acyl substituent in position 3 of the fluoranthene system, and no distinct preference of either *Z*- or *E*-conformations of an acyl substituent in the 8/9 positions. Only *Z*-conformations were further considered for the *O*-protonates and σ-complexes of diacetylfluoranthenes.

The following relative stabilities of the constitutional isomers of acetylfluoranthenes and their derivatives are (i) ketones: $\Delta G_{298}$ = 0.0 kJ/mol ((*Z*)-8-AcFT) and 11.3 kJ/mol ((*Z*)-3-AcFT); (ii) *O*-protonates: $\Delta G_{298}$ = 0.0 kJ/mol ((*Z*)-8-AcFTH$^+$) and 14.71 kJ/mol ((*Z*)-3-AcFTH$^+$); and (iii) σ-complexes: $\Delta\Delta G_{298}$ = 0.0 kJ/mol (3σ-AcFTH$^+$) and 4.4 kJ/mol (8σ-AcFTH$^+$). The relative stabilities of the constitutional isomers of diacetylfluoranthenes are ketones: $\Delta G_{298}$ = 0.0 kJ/mol ((*Z*,*E*)-3,8-$Ac_2$FT), 0.9 kJ/mol ((*Z*,*Z*)-3,9-$Ac_2$FT) (however, in the gas phase $\Delta G_{298}$ = 0.0 kJ/mol ((*Z*,*Z*)-3,9-$Ac_2$FT), and 0.8 kJ/mol ((*Z*,*Z*)-3,8-$Ac_2$FT)); (ii) *O*-3-protonates: $\Delta\Delta G_{298}$ = 0.0 kJ/mol ((*Z*,*Z*)-3,9-$Ac_2$FTH$^+$) and 4.1 kJ/mol ((*Z*,*Z*)-3,8-$Ac_2$FTH$^+$); (iii) *O*-8/9-protonates: $\Delta G_{298}$ = 0.0 kJ/mol ((*Z*,*Z*)-3,9-$Ac_2$FTH$^+$) and 3.4 kJ/mol ((*Z*,*Z*)-3,8-$Ac_2$FTH$^+$); (iv) di-*O*-protonates: $\Delta G_{298}$ = 0.0 kJ/mol ((*Z*,*Z*)-3,9-$Ac_2FTH_2{}^{++}$) and 10.9 kJ/mol ((*Z*,*Z*)-3,8-$Ac_2FTH_2{}^{++}$); (v) σ-complexes: $\Delta G_{298}$ = 0.0 kJ/mol (3,9σ-$Ac_2$FTH$^+$) and 6.4 kJ/mol (3,8σ-$Ac_2$FTH$^+$); (v) *O*-protonated σ-complexes: $\Delta\Delta G_{298}$ = 0.0 kJ/mol (3,9σ-$Ac_2FTH_2{}^{++}$) and 18.4 kJ/mol (3,8σ-$Ac_2FTH_2{}^{++}$).

The proposed mechanism of the Friedel–Crafts acyl rearrangements of acetylfluoranthenes in PPA (Scheme 3) involves deacetylation of 3-AcFT to FT and acetylium ion Ac$^+$ via the protonate 3-AcFTH$^+$ and the σ-complex 3σ-AcFTH$^+$, followed by acetylation at the 8-position to give 8-AcFT via the σ-complex 8σ-AcFTH$^+$ and the protonate 8-AcFTH$^+$.

According to the Hammond–Leffler postulate [46], the relative energies of the transitions states for the formation of the σ-complexes, resemble the relative energies of the σ-complexes. In the case of mono-acetylfluoranthenes, both the ketone 8-AcFT and the *O*-protonate 8-AcFTH$^+$ are lower in relative energies than their respective 3-substituted constitutional isomers (Tables 7 and 8). However, the energy barrier

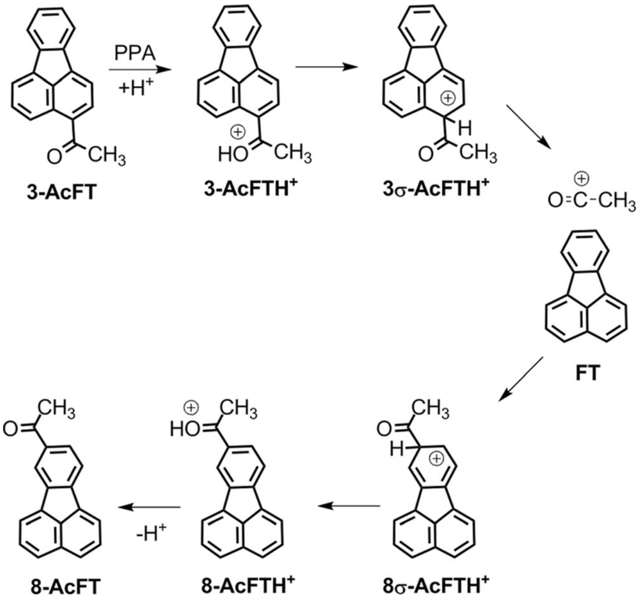
**Table 7** Relative Gibbs-free energies of acetylfluoranthenes and their torsion angles ($\tau$)

| | | $\Delta G_{298}$ (kJ/mol) | $\tau$ (deg) |
|---|---|---|---|
| (*Z*)-3-AcFT | $C_s$ | 11.25 | 0 |
| (*E*)-3-AcFT | $C_1$ | 21.17 | 158 |
| (*Z*)-8-AcFT | $C_s$ | 0.00 | 0 |
| (*E*)-8-AcFT | $C_s$ | 0.85 | 180 |
| (*Z*)-3-AcFTH$^+$ | $C_s$ | 14.71 | 0 |
| (*E*)-3-AcFTH$^+$ | $C_1$ | 24.49 | 169 |
| (*Z*)-8-AcFTH$^+$ | $C_1$ | 1.24 | 0 |
| (*E*)-8-AcFTH$^+$ | $C_s$ | 0.00 | 180 |
| 3σ-AcFTH$^+$ | $C_1$ | 74.02 | −85 |
| 8σ-AcFTH$^+$ | $C_1$ | 78.37 | −177 |

**Table 8** Relative Gibbs-free energies of diacetylfluoranthenes and their torsion angles ($\tau$)

| | | $\Delta G_{298}$ (kJ/mol) | $\tau_3$ (deg) | $\tau_8/\tau_9$ (deg) |
|---|---|---|---|---|
| (*Z*,*Z*)-3,8-$Ac_2FT$ | $C_s$ | 0.41 | 0 | 0 |
| (*Z*,*E*)-3,8-$Ac_2FT$ | $C_s$ | 0.00 | 0 | 180 |
| (*Z*,*Z*)-3,9-$Ac_2FT$ | $C_s$ | 0.90 | 0 | 0 |
| (*Z*,*E*)-3,9-$Ac_2FT$ | $C_s$ | 1.54 | 0 | 180 |
| (*Z*,*Z*)-3H,8-$Ac_2FTH^+$ | $C_1$ | 6.15 | 2 | 0 |
| (*Z*,*Z*)-3H,9-$Ac_2FTH^+$ | $C_s$ | 2.03 | 0 | 0 |
| (*Z*,*Z*)-3,8H–$Ac_2FTH^+$ | $C_1$ | 3.36 | 0 | 0 |
| (*Z*,*Z*)-3,9H–$Ac_2FTH^+$ | $C_s$ | 0.00 | 0 | 0 |
| (*Z*)-3,8σ-$Ac_2FTH^+$ | $C_1$ | 89.88 | 18 | −178 |
| (*Z*)-3,9σ-$Ac_2FTH^+$ | $C_1$ | 83.46 | −1 | 168 |
| (*Z*,*Z*)-3,8-$Ac_2FTH_2^{++}$ | $C_1$ | 10.89 | 2 | 0 |
| (*Z*,*Z*)-3,9-$Ac_2FTH_2^{++}$ | $C_1$ | 0.00 | 2 | 0 |
| (*Z*)-3H,8σ-$Ac_2FTH_2^{++}$ | $C_1$ | 117.38 | 5 | 177 |
| (*Z*)-3H,9σ-$Ac_2FTH_2^{++}$ | $C_1$ | 99.00 | −3 | 172 |

for the formation of the σ-complex 3σ-$AcFTH^+$ is lower than the respective energy barrier leading to 8σ-$AcFTH^+$. The experimental results of the PPA-mediated Friedel–Crafts acyl rearrangements of acetylfluoranthenes demonstrated that 3-AcFT undergoes transformation into 8-AcFT and 3-BzFT gives 8-BzFT, but both 8-AcFT and 8-BzFT yield only FT under the same conditions. Thus, the Friedel–Crafts acyl rearrangements 3-AcFT → 8-AcFT and 3-BzFT → 8-BzFT are thermodynamically controlled processes. Accordingly, 3-AcFT is the kinetically-controlled product, whereas 8-AcFT is the thermodynamically-controlled product. Consistently, deacylation of 3,9-$Ac_2FT$ in PPA gave the more stable isomer 8-AcFT and FT (in addition to the rearrangement product 3-MeBcdFT), whereas 3-AcFT was not identified among the products.



**Scheme 3** Possible mechanisms of 3-AcFT → 8-AcFT acyl rearrangement

In the cases of diacetylfluoranthenes, ketones (*Z*,*E*)-3,8-$Ac_2FT$ and (*Z*,*Z*)-3,9-$Ac_2FT$ have very similar relative energies, whereas 3,9-disubstituted *O*-protonates and σ-complexes have lower relative energies than their respective 3,8-disubstituted constitutional isomers (Tables 7 and 8). The lower relative energies of 3,9-disubstituted diacetylfluoranthenes as compared to 3,8-disubstituted diacetylfluoranthenes are even more pronounced for the di-*O*-protonates and for the mono-*O*-protonated σ-complexes. The experimental results of the $AlCl_3$-mediated Friedel–Crafts acetylation of acetylfluoranthenes demonstrated that both 3-AcFT and 8-AcFT yield only 3,9-$Ac_2FT$. Thus, both kinetic control and thermodynamic control of the Friedel–Crafts acetylations of 3-AcFT and 8-AcFT favor the formation of the constitutional isomer 3,9-$Ac_2FT$.

## Conclusions

Friedel–Crafts acetylation and benzoylation of fluoranthene gave 3-, 8-, and 3,9-acetyl, benzoyl and 4-fluorobenzoylfluoranthene. Friedel–Crafts mono- and diacylation of FT and of acylfluoranthenes and Friedel–Crafts acyl rearrangements of acylfluoranthenes and diacylfluoranthene in PPA proved to be regioselective. Noteworthy is the regioselectivity of acylation of 3-acylfluoranthenes to give 3,9-diacylfluoranthenes, not 3,8-acylfluoranthenes. The acyl rearrangements of monoacylfluoranthenes were not reversible: the kinetically controlled 3-AcFT/3-BzFT rearranged to the thermodynamically controlled 8-AcFT/8-BzFT, whereas the latter did not rearrange to the former. The values of the carbonyl torsion angles of mono- and diacylfluoranthenes derived from the X-ray study, correspond well with their ability to undergo Friedel–Crafts acyl rearrangements. The order of decreasing torsion angles between the carbonyl and the fluoranthene ring system τ is: 7,10-$Ac_2FT$ > 3-BzFT > 3-(4-FBz)FT > 8-BzFT > 3,9-$Ac_2FT$ > 8-AcFT. The regioselectivity and the win of kinetic control over thermodynamic control were supported by the results of the DFT calculations. Furthermore, 3,9-$Ac_2FT$, 3,9-$Bz_2FT$, and 3,9-$(4\text{-}FBz)_2FT$ underwent deacylation in PPA to give 8-AcFT, 8-BzFT, and 8-(4-FBz)FT, respectively. 3-Acylfluoranthenes were not isolated among the acyl rearrangement products of 3,9-diacylfluoranthenes. However, the deacetylation of 3,9-$Ac_2FT$ in PPA gave also the rearrangement product 3-MeB*cd*FT, indicating the formation of 3-AcFT as an intermediate, which then underwent an aldol condensation followed by a Friedel–Crafts cyclization and dehydration. The rich Friedel–Crafts chemistry in PPA in the fluoranthene series is indicated also in the formation of bis(8-fluoranthenyl) ketone from 3-AcFT and 8-AcFT.

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