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Straightforward One-Pot Synthesis of New 4-Phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one Derivatives: X-ray Single Crystal Structure and Hirshfeld Analyses

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Abstract: A straightforward one-pot route for the synthesis of a new 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one is reported form the direct hydrazinolysis of triketo ester and hydrazine hydrate in ethanol. 4-Phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one was subjected to *aza*-Michael addition and *N*-alkylation on reaction with a set of alkylating agents in the presence of K_2CO_3. Hydrazinolysis of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one ester to hydrazide and conversion of hydrazide to thiosemicarbazide were successful. X-Ray single crystals analysis and ^{1}H, ^{13}C NMR were used for unambiguous structure confirmation. The O . . . H, N . . . H, C . . . N and C . . . C in **2**, and the N . . . H, C . . . N, C . . . C, C . . . O and H . . . H interactions in **6** are the most important in the molecular packing based on Hirshfled analysis. Moreover, the presence of short C . . . C and C . . . N contacts in both compounds revealed the presence of π–π stacking interactions.

Keywords: fluoranthenes; polycyclic aromatic heterocycles; *aza*-Michael addition; *N*-alkylation; Hirshfeld Analyses

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1. Introduction

Polycyclic aromatic heterocycles are a class of chemicals include multi-ring aromatic compounds. In particular, fluoranthenes [1–3] are an example of four fused aromatic heterocycles which recentlyreceived a lot of attention, because this core structure has remarkable applications such as organic electronics [4]. Fluoranthene is a building block which was found in many natural products, for example, daldinone E (fungus *Daldinia* sp.) [5], and hortein (which is a fungus *Hortaea werneckii* associated with the sponge *Aplysina aerophoba*) [6]. In a different application of fluoranthenes which was discovered as fluorescent probe (FLUN-550) is a new class of live cell permeant, nontoxic, selective staining and intracellular lipid droplets quantifications based fluoranthenes [7].

Design and synthesis of new substituted of fluoranthenes have been gaining a lot of interest in the last decade. The synthetic roads for this interesting scaffold reported in the literatures though transition metal mediated [8–19] or Diels–Alder reactions [20–23].

Indeed, the palladium compound, $Pd_2(dba)_3$ (20 mol%) was employed as active catalyst for the reaction between 1,8-dichloronaphthalenes and arylboronic acid at elevated temperature (up to 175 °C) to afford the fluoranthenes derivatives [24]. Another approach

that utilized the Pd-catalyst system was achieved for the synthesis of fluoranthenes which proceeded via three steps based on the inter- and intramolecular C-H arylation [25].

The Suzuki−Miyaura reaction also is considered one of the synthetic protocols for the synthesis of fluoranthenes derivatives initiating form 1,8-diiodonaphthalene in the presence of palladium catalysts [26]. Koutentis et al. also explored the chemistry of this interesting scaffold which synthesized the *aza*-analogues by the oxidative and non-oxidative cyclization approach [27]. Other approaches employed the silica sulphuric acid: a reusable solid catalyst for one pot synthesis of densely substituted pyrrole-fused isocoumarins under solvent-free conditions [28].

Recently, Boraei et al. have demonstrated a green and straightforward method for the synthesis of tatraazafluoranthenones starting from ninhydrin and ethyl acetoacetate (β-ketoesters) in water as a green solvent [29].

In this article, we are validating the application of our previous published method and used other β-ketoesters (ethyl benzoylacetate) and ninhydrin for the synthesis of new tatraazafluoranthenone analogues in straightforward, one-pot free catalyst route (Figure 1).

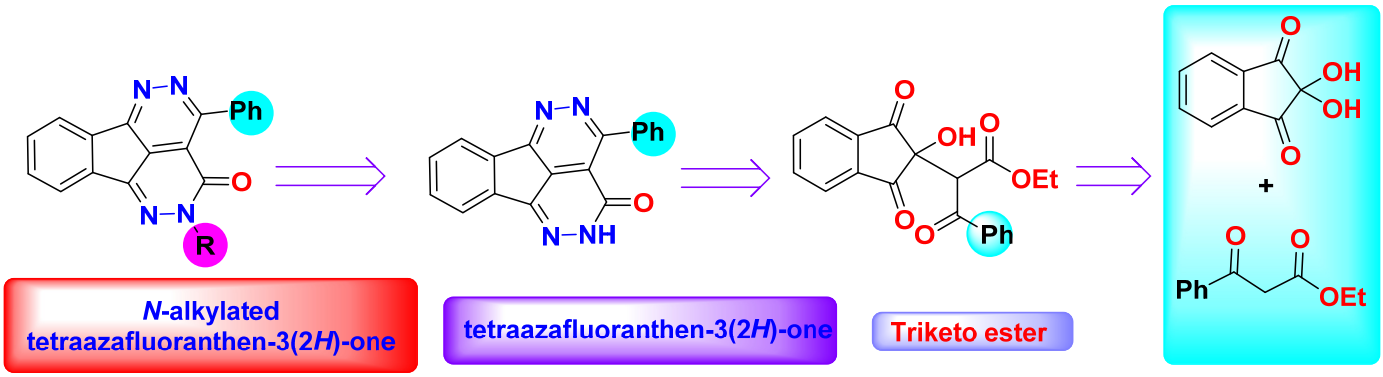


Figure 1. Retro-synthesis of the fluoranthenes.

2. Materials and Methods

General Information

"Stuart Melting Point apparatus [SMP10], Bibby Scientific Ltd., (Wilmington, DE, USA) was used for measuring melting points in open capillaries and were uncorrected. Monitoring of reactions progress was done using TLC Merck aluminum-precoated silica gel plates (60 Å, F_{254}). Product spot visualization was achieved using UV light. NMR spectra were detected using Bruker spectrometer at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR calibrated by (TMS, 0 ppm) as internal standard" (Supplementary Materials).

Synthesis of Ethyl 2-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-3-oxo-3-phenylpropanoate (**1**)

This compound was synthesized and characterized according to the reported procedures [30,31].

Synthesis of 4-Phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one (**2**)

A mixture of triketo ester **1** [6.4 g, 18.2 mmol] and hydrazine hydrate [3.0 mL] was heated under refluxed in ethanol [10.0 mL] until ppt appeared (about 0.5–1 our). The reaction mixture cooled to room temperature and the formed solid was filtered, dried, and recrystallized from DMF/EtOH.

Yield (3.0 g, 55%), m.p. >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.22 (s, 1H), 8.23 (d, J = 6.3 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.9 Hz, 2H), 7.69–7.68 (m, 2H), 7.55–7.54 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.1, 157.9, 157.1, 145.0, 137.3, 135.8, 135.7, 132.9, 131.7, 130.6, 130.4, 128.2, 127.6, 123.8, 123.1, 118.9; Elemental analysis (CHN) calculated for [$C_{18}H_{10}N_4O$]: C, 72.48, H, 3.38, N, 18.78, O, 5.36 found C, 72.61, H, 3.42, N, 18.65.

Michael Addition procedure

A mixture of Michael donor **2** (0.6 g, 2.0 mmol) and Michael acceptor-acrylonitrile (0.12 g, 2.2 mmol) was refluxed in ethanol (10.0 mL) containing Et_3N (0.31 mL, 2.2 mmol) for 6 h. The mixture was cooled, the solid was filtered, and recrystallized from ethanol.

3-(3-Oxo-4-phenyl-1,2,5,6-tetraazafluoranthen-2(3*H*)-yl)propanenitrile (**3**)

Yield (0.55 g, 77%), m.p. 229–230 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (s, 1H), 8.02 (s, 1H), 7.91 (s, 2H), 7.72 (s, 2H), 7.57 (s, 3H), 4.46 (s, 2H), 3.06 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 157.2, 156.7, 144.7, 137.3, 135.5, 133.1, 132.2, 130.6, 130.4, 128.1, 127.2, 124.0, 123.4, 118.9, 118.2, 48.3, 16.9; Elemental analysis (CHN) calculated for [$C_{21}H_{13}N_5O$]: C, 71.79; H, 3.73; N, 19.93, O, 4.55 found C, 71.81; H, 3.83; N, 19.71.

Alkylation procedure

A mixture of tetraazafluoranthen-3(2*H*)-one **2** (0.6 g, 2.0 mmol) and K_2CO_3 (0.3 g, 2.2 mmol), in equal volumes of dry acetone/DMF (10 mL) was stirred for one hour, then alkyl halide (2.2 mmol) was added portion wise, and the reaction mixture was left on stirring overnight (the reaction is monitored by TLC and reflux is fixed if reaction did not complete). Then, the solvent was removed, water was added for complete precipitation and the formed solid was collected by filtration, dried, and recrystallized from EtOH or DMF/EtOH.

2-Allyl-4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one (**4**)

Yield (0.54 g, 79%), m.p. 190–191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34–8.26 (m, 1H), 7.99–7.98 (m, 3H), 7.66–7.54 (m, 5H), 6.13–6.04 (m, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 4.91 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 157.5, 156.3, 144.7, 137.3, 135.5, 134.8, 132.2, 131.8, 131.4, 130.5, 130.3, 128.0, 126.8, 124.00, 123.0, 119.1, 117.6, 55.6; Elemental Analysis calculated for [$C_{21}H_{14}N_4O$]: C, 74.54; H, 4.17; N, 16.56, O, 4.73 found C, 74.69; H, 4.30; N, 16.61.

2-Benzyl-4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one (**5**)

Yield (0.64 g, 83%), m.p. 224–225 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (s, 1H), 8.00 (s, 1H), 7.88 (s, 2H), 7.69 (s, 2H), 7.55 (s, 3H), 7.39 (s, 2H), 7.31 (d, *J* = 19.8 Hz, 3H), 5.41 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.2, 157.3, 156.8, 144.8, 137.4, 137.2, 135.7, 132.9, 132.0, 130.6, 130.3, 128.9, 128.1, 127.9, 127.3, 123.9, 123.3, 118.4, 56.0; Elemental Analysis calculated for [$C_{25}H_{16}N_4O$]: C, 77.30; H, 4.15; N, 14.42, O, 4.12 found C, 77.43; H, 4.21; N, 14.31.

2-Pentyl-4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one (**6**)

Yield (0.45 g, 61%), m.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–8.28 (m, 1H), 7.99–7.97 (m, 3H), 7.65–7.54 (m, 5H), 4.29 (t, *J* = 7.5 Hz, 2H), 1.95–1.74 (m, 2H), 1.41–1.40 (m, 4H), 0.93 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 157.5, 156.4, 144.2, 137.2, 135.7, 134.9, 132.2, 131.3, 130.4, 130.3, 128.0, 126.6, 124.0, 122.8, 117.5, 53.4, 28.9, 28.5, 22.4, 14.0; Elemental analysis (CHN) calculated for [$C_{23}H_{20}N_4O$]: C, 74.98; H, 5.47; N, 15.21, O, 4.34 found C, 75.11; H, 5.63; N, 15.30.

Ethyl 2-(3-oxo-4-phenyl-1,2,5,6-tetraazafluoranthen-2(3*H*)-yl)acetate (**7**)

Yield (0.63 g, 81%), m.p. 189–190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.1 Hz, 2H), 7.99–7.96 (m, 3H), 7.75–7.53 (m, 4H), 4.96 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 158.1, 157.4, 156.8, 145.3, 137.5, 135.2, 134.7, 132.3, 131.8, 130.5, 130.3, 128.0, 127.3, 124.1, 123.2, 117.6, 62.0, 52.8, 14.2; Elemental Analysis calculated for [$C_{22}H_{16}N_4O_3$]: C, 68.74; H, 4.20; N, 14.58, O, 12.49 found C, 68.88; H, 4.14; N, 14.41.

Synthesis of 2-(3-Oxo-4-phenyl-1,2,5,6-tetraazafluoranthen-2(3*H*)-yl)acetohydrazide (**8**)

Tetraazafluoranthen-3(2*H*)-one ethyl ester **7** (0.77 g, 2.0 mmol) and hydrazine hydrate 80% (2.0 mL) was refluxed in ethanol (10 mL) for 2 hours, left to cool, the formed solid product was collected by filtration, dried, and recrystallized from EtOH.

Yield (0.67 g, 90%), m.p. 287–288 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 8.30–8.27 (m, 1H), 8.04–8.02 (m, 1H), 7.90–7.87 (m, 2H), 7.74–7.72 (m, 2H), 7.62–7.51 (m, 3H), 4.81 (s, 2H), 4.31 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.3, 158.2, 156.9, 144.8, 137.3, 135.5, 133.1, 132.2, 130.6, 130.5, 128.2, 127.5, 124.0, 123.4, 118.3, 55.0; Elemental Analysis calculated for [$C_{20}H_{14}N_6O_2$]: C, 64.86; H, 3.81; N, 22.69, O, 10.91 found C, 64.99; H, 3.93; N, 22.61.

Synthesis of 2-(2-(3-Oxo-4-Phenyl-1,2,5,6-tetraazafluoranthen-2(3*H*)-yl)acetyl)-N-phenylhydrazine-1-carbothioamide (**9**)

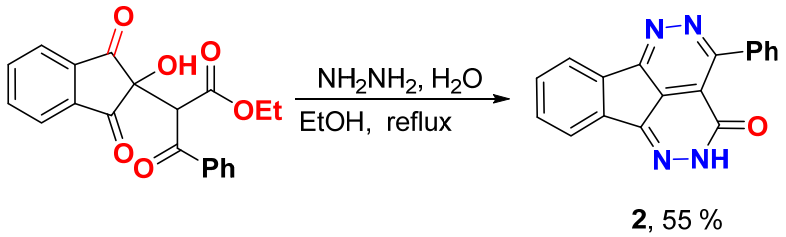
To the tetraazafluoranthene-hydrazide **8** (0.74 g, 2.0 mmol) in ethanol (10 mL), phenyl isothiocyanate (0.26 mL, 2.2 mmol) was added. The mixture was refluxed for 4 hours, then cooled. The solid product was collected by filtration, dried, and recrystallized from DMF/EtOH.

Yield (0.82 g, 82%), m.p. >300 ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 9.82 (s, 1H), 9.36 (brs, 1H), 8.31–8.29 (m, 1H), 8.10–7.95 (m, 1H), 7.94–7.87 (m, 2H), 7.79–7.69 (m, 2H), 7.66–7.50 (m, 3H), 7.41–7.39 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 5.03 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 181.0, 166.9, 158.1, 157.2, 157.0, 144.8, 139.3, 137.2, 135.4, 133.1, 132.2, 130.6, 128.6, 128.2, 127.2, 125.6, 124.0, 123.4, 118.0, 55.6; Elemental Analysis calculated for [$C_{27}H_{19}N_7O_2S$]: C, 64.15; H, 3.79; N, 19.39; O, 6.33; S, 6.34 found C, 64.31; H, 3.71; N, 19.29; S, 6.37.

3. Results and Discussion

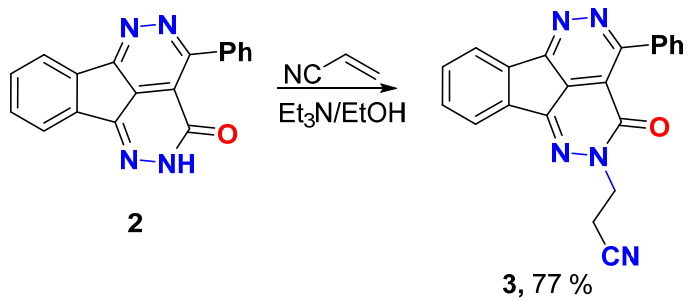
3.1. Chemistry

Hydrazinolysis of triketo ester **1** by hydrazine hydrate in ethanol under reflux for 0.5-1 h, fascinatingly, gave 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one **2** in moderate yield (55%) (Scheme 1). The ^{1}H NMR displayed, in addition to the aromatic proton signals between δ 8.23 and 7.55 ppm, a signal at δ 13.22 ppm for NH. The ^{13}C NMR showed all carbons between δ 158.1 and 118.9 ppm.



Scheme 1. Synthesis of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one **2**.

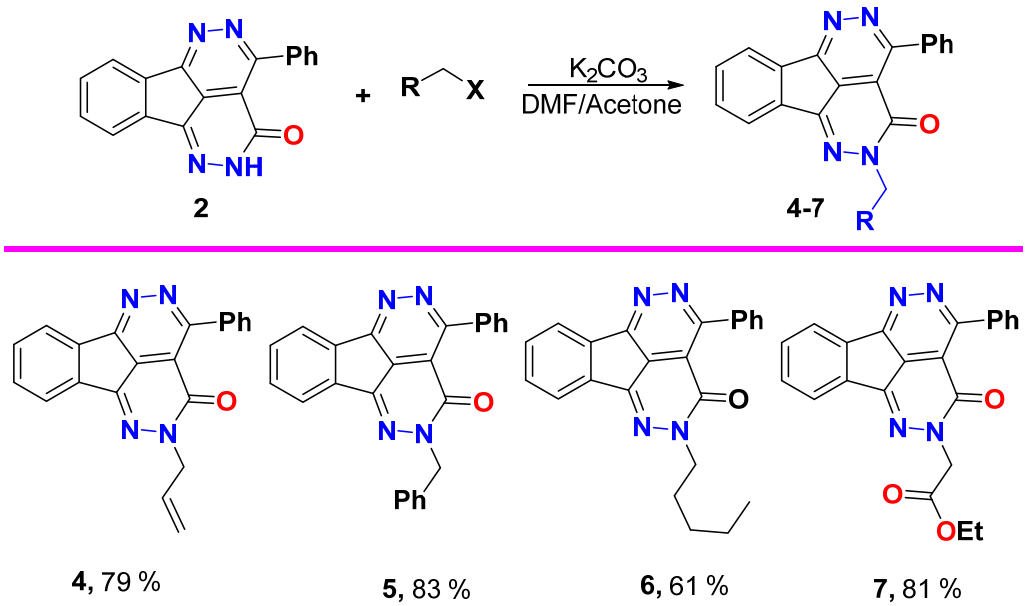
Aza-Michael addition was explored from the addition of **2** to acrylonitrile in ethanol and the presences of Et_3N to give the Michael adduct **3** in good yield (Scheme 2). The Michael adduct revealed two new signals at δ 4.46 and 3.06 ppm in ^{1}H NMR and their respective carbons appeared at δ 48.3 and 16.9 ppm in ^{13}C NMR which strongly support *aza*-Michael addition, not *oxa*-Michael addition.



Scheme 2. *Aza*-Michael addition of compound **2** to acrylonitrile.

Alkylation of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one **2** with allyl bromide, benzyl bromide, amyl bromide, and ethyl chloroacetate was done in acetone/DMF and use of K_2CO_3 as proton capturer which led to *N*-alkylation and formation of *aza*-alkylated products **4–7** in good yields (Scheme 3). The allylated product **4** spectra demonstrated that the allyl group protons as: The sp^2 vinylic methine proton CH_2=**CH-** appeared as multiplet between 6.13 and 6.14 ppm, the vinylic sp^2 methylene protons **H_2C**=CH- were found as two doublet signals, one of them at 5.37 ppm with coupling constant value 17.2 Hz for

the trans proton, and the other was deduced at 5.30 ppm with ^{3}J value 10.2 Hz for the cis proton. The allylic sp^{3} methylene protons **NCH$_2$** was established as doublet at 4.91 ppm. The allylic carbon atom **NCH$_2$** was detected at δ 55.6 ppm. The benzylated compound **5** showed the benzyl methylene protons as singlet at 5.41 ppm and the corresponding benzylic methylene carbon at δ 56.0 ppm. The amylated tetraazafluoranthen-3(2*H*)-one **6** showed the amyl group protons at δ 4.29, 1.95–1.74, 1.41–1.40, and 0.93 ppm and the respective amyl carbons at δ 53.4, 28.5, 22.4, and 14.0 ppm. The esterified product **7** showed a singlet signal at 4.96 ppm for **NCH$_2$,** a quartet signal at δ 4.29 ppm for **OCH$_2$**, and a triplet signal at δ 1.26 ppm for CH$_3$. The ^{13}C NMR displayed the carbonyl carbon of the ester group at δ 168.0 ppm, the **OCH$_2$** at 62.0 ppm, **NCH$_2$** at δ 52.8 ppm, and CH$_3$ at δ 14.2 ppm.

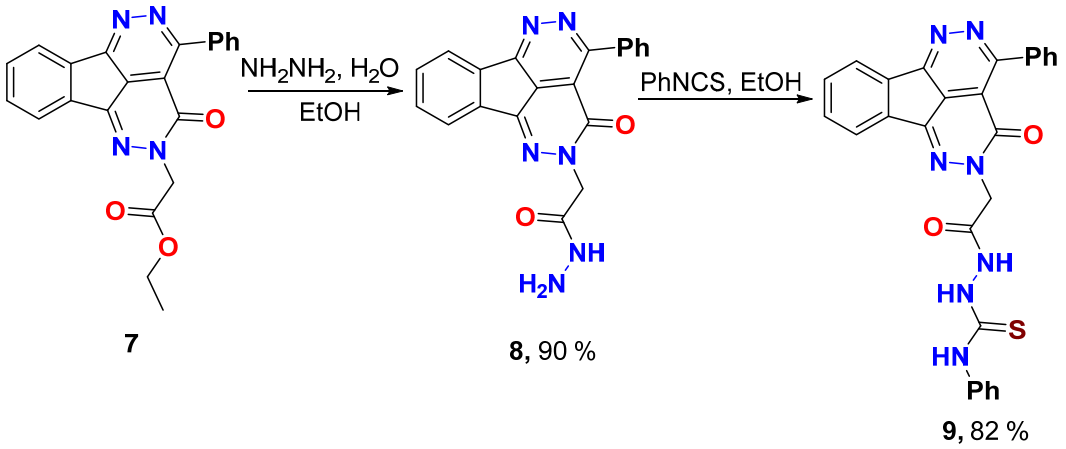


Scheme 3. *Aza*-alkylation of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one**2** with a set of alkylating agents.

Reaction of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one ester **7** with hydrazine hydrate afforded the hydrazide **8** which was subjected to reaction with phenyl isothiocyanate in ethanol to afford the thiosemicarbazide **9** (Scheme 4). The 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one hydrazide **8** displayed the hydrazide group protons at δ 9.26 and 4.31 ppm for **NH** and **NH$_2$**, respectively, in addition to the **NCH$_2$** protons at δ 4.81 ppm. The ^{13}C NMR showed the carbonyl carbon of the hydrazide group at δ 166.3 ppm and the **NCH$_2$** methylene carbon at δ 55.0 ppm. The 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one thiosemicarbazide **9** showed the three NH protons signals at δ 10.40, 9.82, and 9.36 ppm. The respective ^{13}C NMR detected the thiocarbonyl carbon (C=S) at δ 181.0 ppm, the carbonyl carbon (C=O) at δ 166.9 ppm, and the **NCH$_2$** methylene carbon at δ 55.6 ppm.

3.2. X-ray Discerption of Compounds **2** *and* **6**

The X-ray structure of **2** is presented in Figure 2A. The structure of **2** crystallized in the orthorhombic crystal system and *Pbca* space group with lattice parameters: a = 12.82600(10) Å, b = 7.80290(10) Å and$c$ = 26.6306(2) Å, and unit cell volume of 2665.19(4) Å3 and Z = 8 (Table 1). There are four fused ring systems which are almost coplanar. The phenyl ring attached to this fused system is twisted from its mean plan by 47.96°Selected geometric parameters of **2** are listed in Table 2.



Scheme 4. Hydrazinolysis of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one ester and thiosemicarbazide formation.

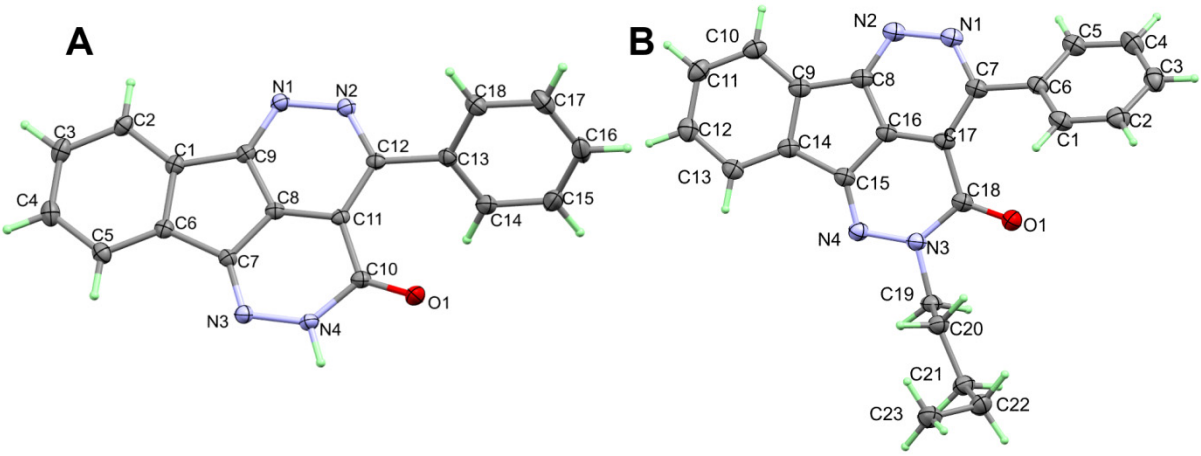


Figure 2. ORTEP of compounds **2** (**A**) and **6** (**B**).

The supramolecular structure of **2** is dominated by the N4-H4 . . . N1 hydrogen bonding interactions leading to the hydrogen bonding polymer shown in the upper part of Figure 2. The hydrogen bond parameters are listed in Table 3. In addition, the hydrogen bonded chains are stacked to each other via significant amount of π–π contacts. The shortest π–πstacking interactions are listed in Table 4. Hence, the supramolecular structure of **2** could be described by 1D hydrogen bonding polymer along the b-direction (Figure 3; upper part) combined with π–π stacking interactions along the a-direction (Figure 3; lower part).

The X-ray structure of **6** is presented in Figure 2B. The structure of **6** crystallized in the less symmetric monoclinic crystal system and $P2_1/c$ space group with lattice parameters: a = 5.26840(10) Å, *b* = 15.21900(10) Å, *c* = 22.7155(2)Å, $\alpha = \gamma = 90$ while $\beta = 93.6920(10)$ and unit cell volume of 1817.54(4) Å3 and Z = 4. Selected geometric parameters of **6** are listed in Table 2. In this case, the mean plane of the almost coplanar fused ring system and the phenyl ring attached to it are twisted from one another by 40.66°. The value of the twist angle is less than that in **2**. The packing in 6 is dominated by π–π stacking interactions shown in Figure 4 and the shortest interactions between the stacked π-system are listed in Table 4.

Table 1. Crystal data of **2** and **6**.

Identification Code	2	6
CCDC	2,129,954	2,129,955
empirical formula	$C_{18}H_{10}N_4O$	$C_{23}H_{20}N_4O$
Fw	298.30	368.43
temp (K)	120(2) K	120(2)
λ(Å)	1.54184 Å	1.54184
Cryst. Syst.	Orthorhombic	Monoclinic
space group	*Pbca*	$P2_1/c$
a (Å)	12.82600(10)	5.26840(10)
b (Å)	7.80290(10)	15.21900(10)
c (Å)	26.6306(2)	22.7155(2)
α, β, γ (deg)	$\alpha = \beta = \gamma = 90$	$\alpha = \gamma = 90$; $\beta = 93.6920(10)$
V (Å^3)	2665.19(4)	1817.54(4)
Z	8	4
ρ_{calc} (Mg/m^3)	1.487	1.346
μ(Mo Kα) (mm^{-1})	0.787	0.677
No. reflns.	37,511	46,295
Unique reflns.	2802	3840
Completeness to θ = 67.684°	100%	100%
GOOF (F^2)	1.057	1.052
R_{int}	0.0290	0.0377
R_1 [a] ($I \geq 2\sigma$)	0.0328	0.0356
wR_2 [b] ($I \geq 2\sigma$)	0.0958	0.0901

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for **2**.

2	
O(1)-C(10)	1.2109(12)
N(1)-C(9)	1.3153(13)
N(1)-N(2)	1.3726(12)
N(2)-C(12)	1.3361(13)
N(3)-C(7)	1.3034(14)
N(3)-N(4)	1.3660(12)
N(4)-C(10)	1.4089(12)
6	
O(1)-C(18)	1.2207(13)
N(1)-C(7)	1.3415(13)
N(1)-N(2)	1.3709(12)
N(2)-C(8)	1.3168(13)
N(3)-N(4)	1.3716(12)
N(3)-C(18)	1.4137(13)
N(3)-C(19)	1.4696(12)

Table 3. Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4)...N(1)#1	0.927(18)	1.992(18)	2.9135(12)	172.3(13)
Symmetry code: #1 x, y−1, z				

Table 4. π–π stacking for **2** and **6** [Å and °].

Contacts	Length	Contacts	Length
2		**6**	
C1 . . . C7	3.387	N2 . . . C5	3.195
C1 . . . C8	3.378	C11 . . . C8	3.344
C3 . . . C10	3.334	C12 . . . C15	3.303
C6 . . . C9	3.337	C14 . . . C18	3.301

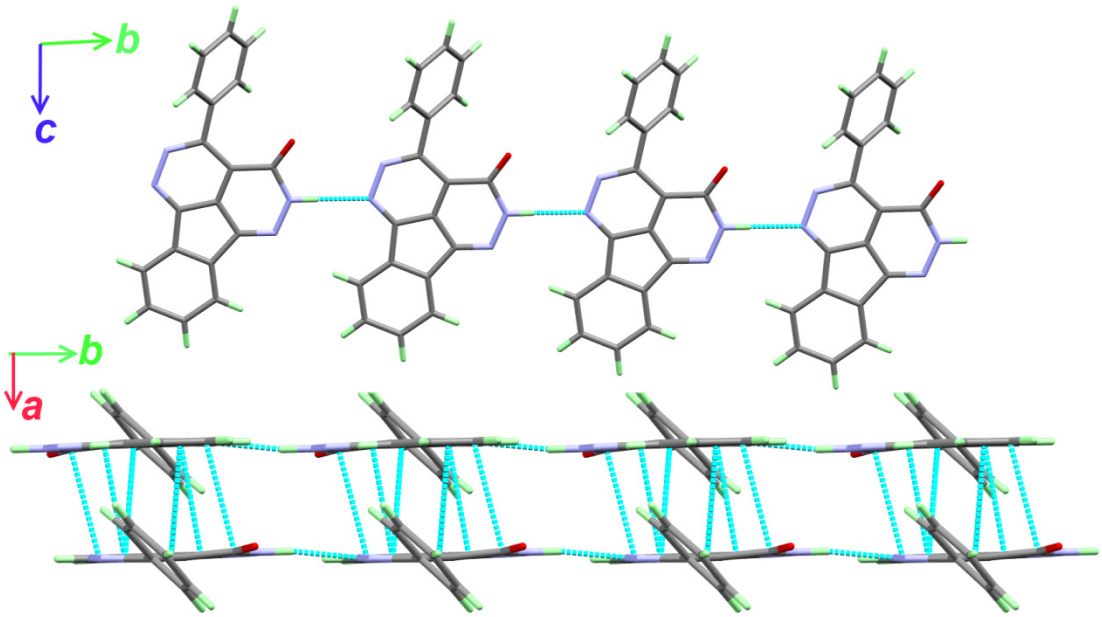


Figure 3. Packing via N-H . . . N hydrogen bonds and π–π stacking (lower) in **2**.

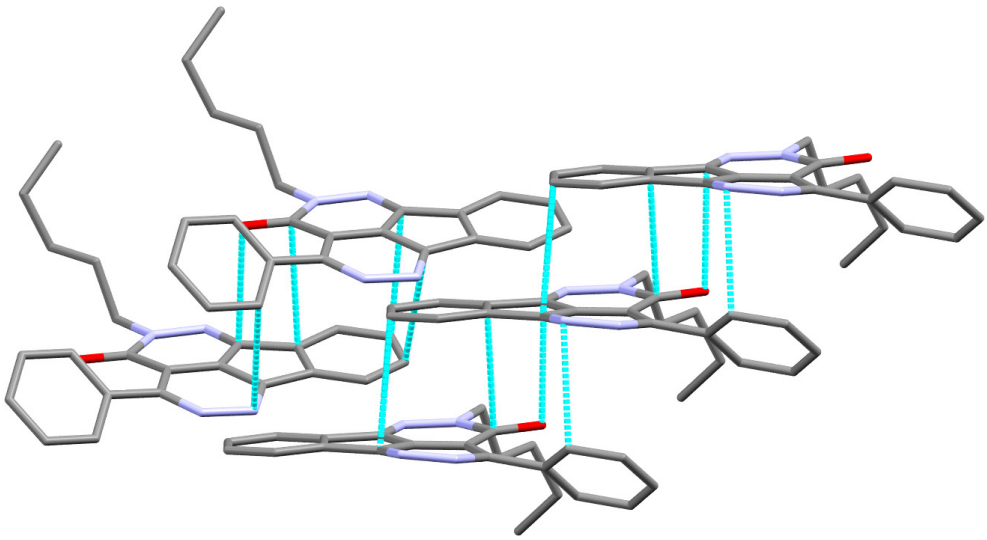


Figure 4. π–π stacking (lower) in **2**.

3.3. Analysis of Molecular Packing

Each crystal has its characteristic Hirshfeld surfaces which shed the light on the important intermolecular interactions which play important role in the crystal stability. In Figure 5, the different mapped surfaces of compounds **2** and **6** are summarized. The d_{norm} indicated a number of red spots related to intermolecular contacts shorter than the vdWs radii sum of the interacting atoms. In compound **2**, the most important contacts are

the O . . . H, N . . . H, C . . . N and C . . . C interactions. On the other hand, the N . . . H, C . . . N, C . . . C, C . . . O and H . . . H interactions are the most important. Summary of these short contacts and the corresponding interaction distances are depicted in Table 5. The results revealed very well the presence of large number of C . . . C and C . . . N contacts in both compounds which confirm the presence of π–π stacking interactions. Generally, these contacts occurred at longer interaction distances in **2** compared to **6**. In addition, the red/blue triangles in the shape index and large green area in curvedness are other evidences on the presence of π–π stacking interactions (region D in Figure 5).

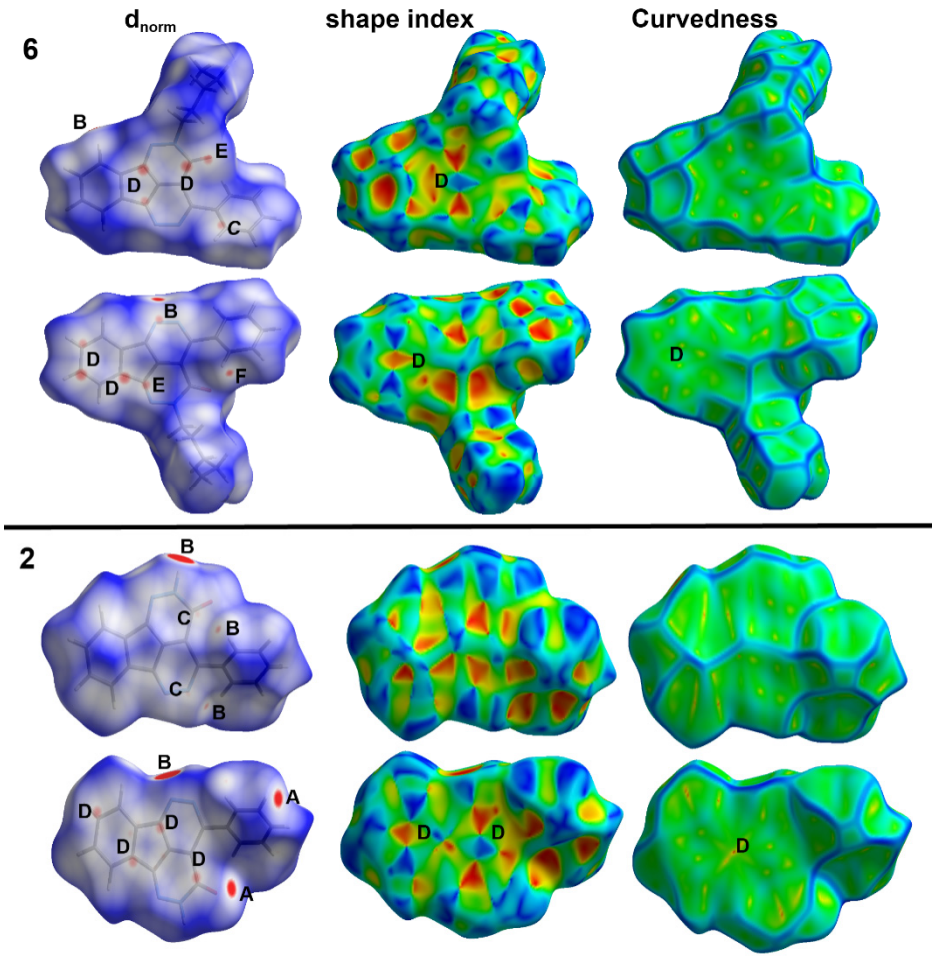


Figure 5. Hirshfeld maps of compounds **2** and **6**. The most important interactions are (A) O . . . H, (B) N . . . H, (C) C . . . N, (D) C . . . C, (E) C . . . O, and (F) H . . . H.

Table 5. Short contacts in compounds **2** and **6**.

Contact	Distance	Contact	Distance
2		**6**	
N1 . . . H1	1.911	N2 . . . H13	2.446
N2 . . . H14	2.584	C5 . . . N2	3.195
O1 . . . H17	2.405	C11 . . . C8	3.344
C10 . . . N2	3.227	C12 . . . C15	3.303
C1 . . . C7	3.387	C14 . . . C18	3.301
C1 . . . C8	3.378	C15 . . . O1	3.158
C3 . . . C10	3.334	H1 . . . H1	2.108
C6 . . . C9	3.337		

On the other hand, analysis of the fingerprint plot gave a quantitative summary for all intermolecular contacts occurred in the crystal structure of compounds **2** and **6** (Figure 6).The decomposition of the fingerprint plot gave a quantitative summary for all contacts that occurred in the crystal structures of compounds **2** and **6** (Figure 7). It is clear that the most frequent contacts in both compounds are the H . . . H interactions. The percentages of H . . . H interactions are 53.6 and 32.4% in compounds **2** and **6**, respectively. The shortest H . . . H contacts in **6** are H1 . . . H1 with interaction distance of 2.108 Å. In **2**, all H . . . H contacts are significantly long and are considered of less importance compared to compound **6**. The second most frequent contacts are the C . . . H interactions which comprised 15.9 and 23.1% from the whole interactions occurred in the crystal of **2** and **6**, respectively. In compound **2**, the percentages of the important O . . . H, N . . . H, C . . . N and C . . . C interactions are 3.5%, 13.6%, 2.2%, and 8.3%, respectively. Both O . . . H and N . . . H contacts appeared as sharp spikes in the fingerprint plot (Figure 6). As a result, these interactions are considered strong and play an important role in the crystal stability of **2** and the π–π stacking interactions as well. The spikes of the N . . . H and O . . . H interactions in **6** are less sharp, indicating weaker interactions than those that occurred in **2**. The percentages of the O . . . H, N . . . H, C . . . N and C . . . C interactions in **6** are 9.0, 15.8, 7.3, and 9.1%, respectively.

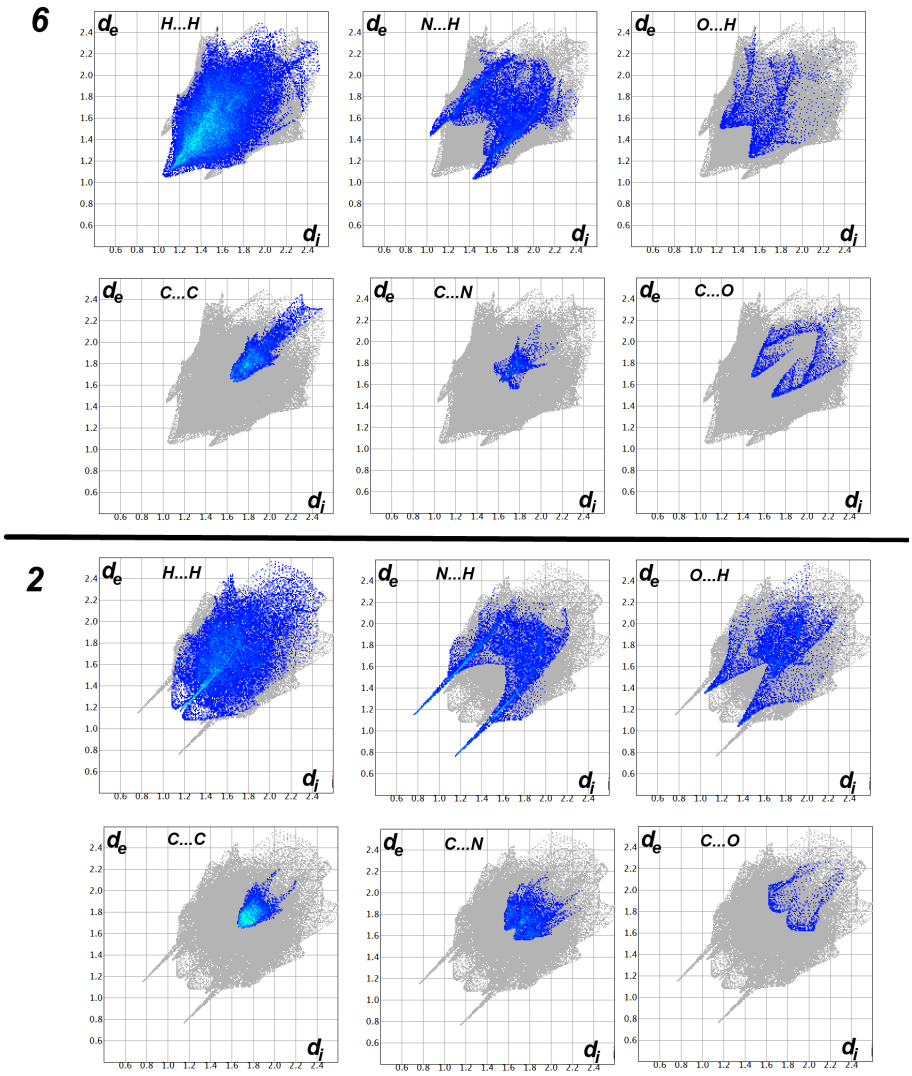


Figure 6. Decomposed fingerprint plots in compounds **2** and **6**.

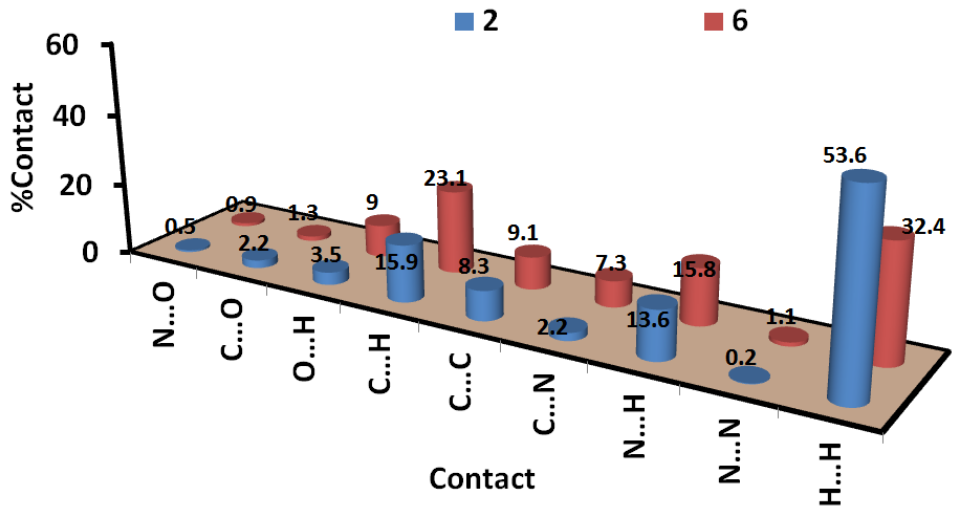


Figure 7. All intermolecular interactions in compounds **2** and **6**.

4. Conclusions

In conclusion, this manuscript introduced a direct one-pot method for obtaining 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one from triketo ester to validate the application of our previous published method. Herein, another *β*-ketoester (ethyl benzoylacetate) was used for obtaining the triketo ester which used for the synthesis of tatraazafluoranthenone. On reaction with Michael acceptors like acrylonitrile, *aza*-Michael addition was produced. Alkylation of tetraazafluoranthen-3(2*H*)-one in the presence of K_2CO_3 led to *N*-alkylation, not *O*-alkylation, this evidence was deduced from the ^{13}C NMR signal around 50.00 ppm for NCH_2. Hydrazinolysis of 4-phenyl-1,2,5,6-tetraazafluoranthen-3(2*H*)-one ester led to hydrazide formation which is converted to thiosemicarbazide by reaction with phenyl isothiocyanate. Different intermolecular interactions that occurred in the crystal structures of compound **2** and **6** were analyzed using Hirshfled calculations.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12020262/s1, X-ray structure determinations; Figure S1: ^1H NMR of **2**; Figure S2: ^{13}C NMR of **2**; Figure S3: ^1H NMR of **3**; Figure S4: ^{13}C NMR of **3**; Figure S5: ^1H NMR of **4**; Figure S6: ^{13}C NMR of **4**; Figure S7: ^1H NMR of **5**; Figure S8: ^{13}C NMR of **5**; Figure S9: ^1H NMR of **6**; Figure S10: ^{13}C NMR of **6**; Figure S11: ^1H NMR of **7**; Figure S12: ^{13}C NMR of **7**; Figure S13: ^1H NMR of **8**; Figure S14: ^{13}C NMR of **8**; Figure S15: ^1H NMR of **9**; Figure S16: ^{13}C NMR of **9**.

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