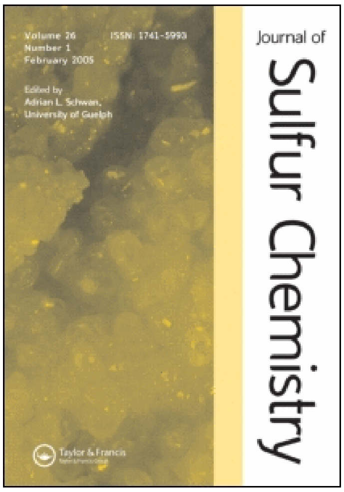

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Ionic liquids as green and recyclable solvents for the synthesis of *N*-substituted *N*′-aroylthioureas containing 9,10-anthraquinone moiety

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Ionic liquids as green and recyclable solvents for the synthesis of *N*-substituted *N′*-aroylthioureas containing 9,10-anthraquinone moiety

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The reaction of aroyl isothiocyanates with 1-aminoanthraquinone or 2-aminoanthraquinone in ionic liquids leads to an efficient synthesis of *N*-substituted *N′*-aroylthioureas, containing 9,10-anthraquinone moiety, in 70–95% yields. All of the pigments were fully characterized by ^{1}H NMR, ^{13}C NMR, IR, and UV–vis absorption spectra.

Keywords: ionic liquid; 1-aminoanthraquinone; disperse dye; aroyl isothiocyanate; green chemistry

1. Introduction

Ionic liquids (ILs) have gained tremendous attention in the last 15 years (*1–3*). They are, among other uses, solvents and are frequently fitted with attributes like ‘modern’, ‘green’, ‘designable’, ‘non-volatile’, ‘non-coordinating’, etc.; although, it is increasingly recognized that none of these labels should be used lightly. Nonetheless, many chemical reactions have been attempted and successfully performed in IL media, and oftentimes these systems show interesting and peculiar features. Yet, considerable work in IL chemistry is still based on trial-and-error rather than fundamental understanding and rational design. To rationalize the differences between ILs and molecular solvents, it is important to understand their properties (*1–6*). Aminoanthraquinones are the basic structural units of the disperse dyes (*6–12*), characterized by good fastness properties and brightness. They provide bright red to blue shades. In this group, acylamino-anthraquinones are included, which possess mainly yellow and orange colors. Anthraquinone derivatives having thiourea group have been employed as colorimetric sensors (*13–15*).

In continuation of our current interest in the development of new routes to modified 9,10-anthraquinones (*16–18*), herein we report a simple synthesis of *N*-substituted *N′*-aroylthioureas containing 9,10-anthraquinones as disperse dyes in ILs as novel and recyclable solvents.

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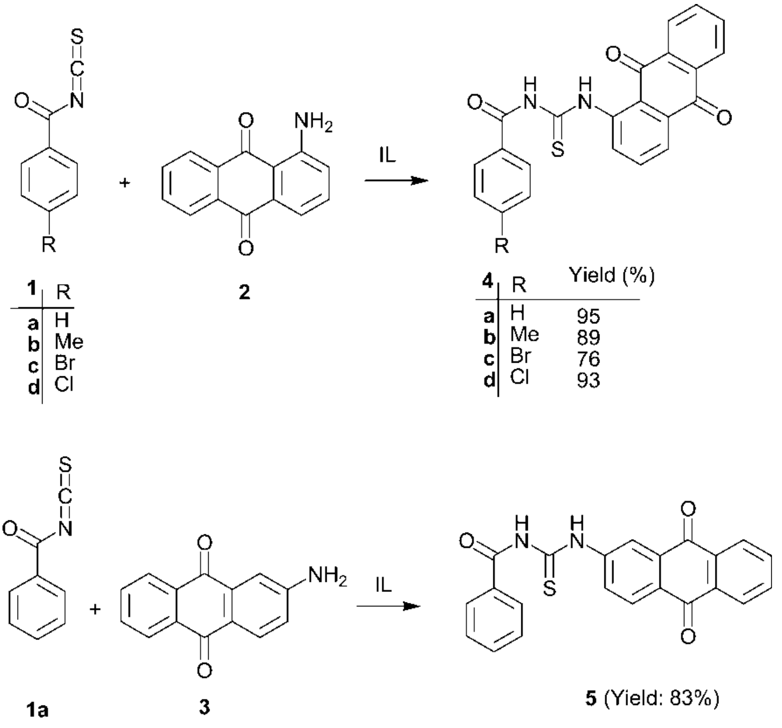
2. Results and discussion

2.1. *Structural characterization of disperse dyes*

The reaction of benzoyl isothiocyanates **1** with 1-aminoanthraquinone (1-AAQ, **2**) or 2-aminoanthraquinone (2-AAQ, **3**) in different ILs at room temperature, led to *N*-substituted *N*-aroylthioureas **4** or **5** containing 9,10-anthraquinone moiety in 76–95% yields (Scheme 1). Under similar conditions, terephthaloyl isothiocyanate (**6**) reacted with **2** or **3** to afford product **7** or **8** in good yields (Scheme 2).



1	R
a	H
b	Me
c	Br
d	Cl

2

4	R	Yield (%)
a	H	95
b	Me	89
c	Br	76
d	Cl	93

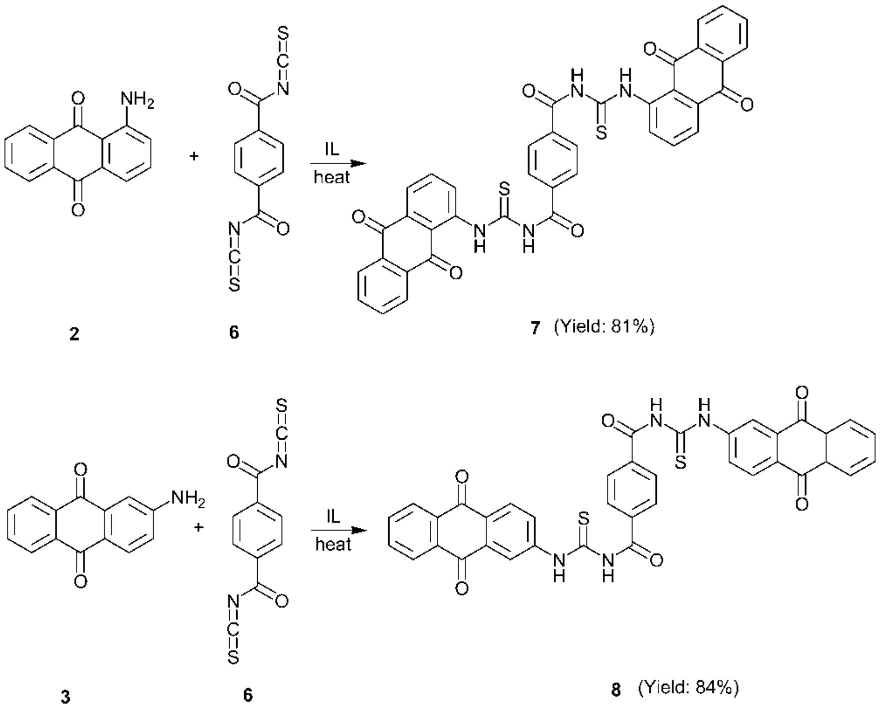
1a **3** **5** (Yield: 83%)

Scheme 1. Preparation of compounds **4** and **5**.

The ILs bearing different cations and anions (Scheme 3) have been synthesized in order to check both the commonly used ILs with unsymmetrical 1-methyl-3-alkylimidazolium cations and symmetrical 1,3-dialkylimidazolium cations with counter ions such as Br^-, BF_4^-, PF_6^-, Cl^-, or HSO_4^-.

An initial reaction of 1-AAQ or 2-AAQ and aroyl isothiocyanates **1** was carried out under different conditions. The results indicated that the symmetrical IL **12** exhibited excellent yield. In contrast, low yields were obtained in ILs containing a PF_6^- counter ion, which can be attributed to the poor solubility of 1-AAQ or 2-AAQ in the hydrophobic IL [bmim][PF_6]. When the reactions were carried out in dimethyl formamide (DMF), low yields were observed, except for the reaction of 1-AAQ and IL **12**.

The influence of IL structure on the yield of dyes was studied. A comparison of the data in Table 1 for ILs **12** and **14** (Scheme 3), shows that the best results were obtained in symmetrical IL **12**. The influence of the IL alkyl chain length on the yields of the products was investigated using ILs with alkyl chains of $n = 3$, 4, or 8 carbon atoms. The reaction occurred in homogeneous



Scheme 2. Preparation of compounds **7** and **8**.

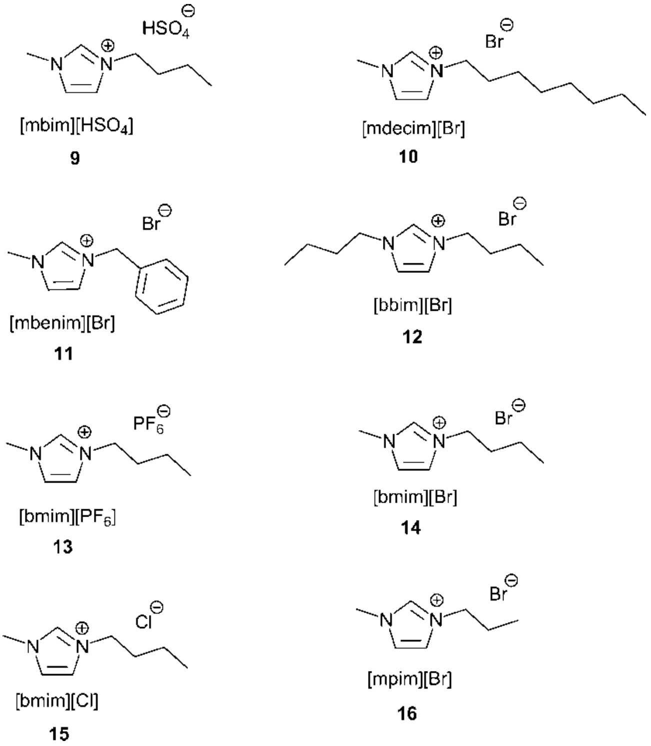
solution for ILs with $n = 4$, with good results. The use of hydrophobic ILs such as **13** in the synthesis of dyes did not give satisfactory results.

The structures of dyes were deduced from their elemental analyses and from their high-field ^{1}H- and ^{13}C NMR, IR, and UV–vis spectra and thermal gravimetric (TG) measurements. The ^{1}H NMR spectrum of **4a** in dimethylsulfoxide (DMSO)-d_6 showed two singlets ($\delta = 11.71$ and 13.84 ppm)

Table 1. Reaction conditions for the preparation of compounds **4** and **7**.

Product	Reaction medium	Yield (%)[a]	Temperature (°C)
4a	DMF[b]	40	60
4a	**9**	55	60
4a	**10**	78	80
4a	**11**	80	80
4a	**12**	98	60
4a	**13**	56	60
4a	**14**	86	60
4a	**15**	88	60
4a	**16**	85	60
7	DMF[b]	45	60
7	**9**	46	60
7	**10**	62	60
7	**11**	74	60
7	**12**	81	60
7	**13**	53	60
7	**14**	87	60
7	**15**	89	60
7	**16**	74	60

[a] Aroyl isothiocyanates = 1.0 mmol; 1-aminoanthraquinone = 1.0 mmol; reaction time = 5 h.
[b] DMF = 10 cm^3.



Scheme 3. The structures of the ILs used in this study.

for the NH groups, along with multiplets for the aromatic ($\delta = 7.00$–9.80 ppm) protons. The ^{13}C NMR spectra of **4** and **5** showed signals in agreement with the proposed structure. Partial assignments of these resonances are given in Section 4 and Tables 1 and 2.

The ^{1}H- and ^{13}C NMR spectra of **4b–d**, **5**, **7**, or **8** are similar to those for **4a**, except for the aromatic moieties, which exhibited characteristic signals with appropriate chemical shifts (Table 3).

The UV–vis absorption spectra of **4** and **5** are shown in Figure 1, and those of **7** and **8** in Figure 2.

2.2. *TGA analyses*

Thermal gravimetric analyses (TGA) were used in order to investigate the thermal properties of the dyes **4**, **5**, and **7**. Some thermal regions are important in the TGA of these dyes, which include the initial decomposition temperature (IDT), the dye decomposition temperature (DDT),

Table 2. Experimental and characterization data of compounds **4**, **5**, **7**, and **8**.

Compound	λ_{max} (nm)	Yield (%)[a]	Color and appearance	Melting point (°C)
4a	210, 425	95	Yellow powder	213
4b	300, 375	89	Yellow powder	229
4c	225, 500	76	Red-orange solid	195
4d	320, 510	93	Red-orange solid	210
5	308	83	Red-brown solid	230
7	290, 575	81	Green powder	295
8	310	84	Shiny green powder	285

[a] Aroyl isothiocyanates = 2.0 mmol; 2-aminoanthraquinone = 1.0 mmol; under optimum conditions.

Table 3. Analytical and spectral data of compounds **4**, **5**, **7**, and **8**.

			Elemental analysis						
			Required (%)			Found (%)			
Compound	Formula	Molecular weight	C	H	N	C	H	N	IR (KBr, cm^{-1})
4a	$C_{22}H_{14}N_2O_3S$	386.4	68.38	3.65	7.25	68.2	3.60	7.22	1153 (C=S), 1577 (C=O), 1660 (C=O), 3400 (N−H)
4b	$C_{23}H_{16}N_2O_3S$	400.4	68.98	4.03	7.00	68.94	4.00	7.05	1159 (C=S), 1577 (C =O), 1667 (C=O), 3425 (N−H)
4c	$C_{22}H_{13}BrN_2O_3S$	465.3	56.79	2.82	6.02	56.88	2.86	6.10	1147 (C=S), 1574 (C=O), 1665 (C=O), 3468 (N−H)
4d	$C_{22}H_{13}ClN_2O_3S$	420.5	62.78	3.09	6.65	62.85	3.12	6.68	1173 (C=S), 1577 (C=O), 1667 (C=O), 3418 (N−H)
5	$C_{22}H_{14}N_2O_3S$	386.4	68.38	3.65	7.25	68.41	3.63	7.28	1185 (C=S), 1574 (C=O), 1675 (C=O), 3200 (N−H)
7	$C_{38}H_{22}N_4O_6S_2$	694.7	65.70	3.19	8.06	65.73	3.21	8.00	1154 (C=S), 1577 (C=O), 1659 (C=O), 1686 (C=O), 3418 (N−H)
8	$C_{38}H_{22}N_4O_6S_2$	694.7	65.70	3.19	8.06	65.78	3.16	8.09	1161 (C=S), 1188 (C=S), 1655 (C=O), 1628 (C=O), 1599 (C=O), 3268 (N−H), 3415 (N−H)

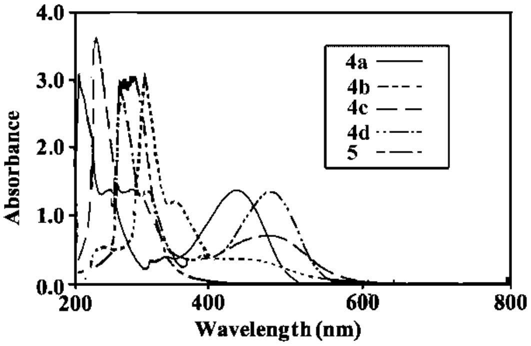


Figure 1. The UV–vis absorption spectra of **4** and **5**, measured in DMF at a concentration of 0.08 mmol dm^{-1}.

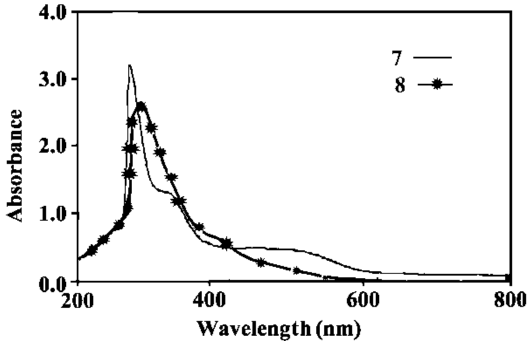


Figure 2. The UV–vis absorption spectra of **7** and **8**, measured in DMF at a concentration of 0.08 mmol dm^{-1}.

the maximum dye decomposition temperature (DDT$_{max}$), and the yield percent at 500 °C. DDT corresponds to the temperature at which 10% weight loss occurred for dye, and DDT$_{max}$ corresponds to the temperature at which the maximum rate of weight loss occurs. These values are listed in Table 4 for dyes **4**, **5**, and **7**. Figure 3 shows the TGA values for these dyes. The IDT values lied in the range of 204–295 °C in inert atmosphere. Thus, **7** (IDT = 295 °C) is expected to have the highest thermal stability. On the other hand, if DDT values are considered as the thermal stability criterion, **4a** will be the most thermally stable dye. It is preferred that all the three regions of the TGA curves are considered. The symmetrical compound **7** has the highest values of IDT, DDT, and DDT$_{max}$, and it is expected to be the most thermally stable among the dyes studied in this work.

Table 4. Thermal properties of dyes **4**, **5**, and **7**.

Dyes	IDT[a] (°C)	DDT[b] (°C)	DDT$^{c}_{max}$ (°C)	Char yield[d](%)
4a	234	266	325	58
4b	240	280	355	52
4c	204	240	350	55
4d	200	245	325	50
5	240	260	350	57
7	295	345	520	63

[a] Initial decomposition temperature.

[b] Dye decomposition temperature at 10% weight loss.

[c] Maximum dye decomposition temperature.

[d] Percentage weight of material left undecomposed after TGA analysis at the maximum temperature of 500°C at heating rate of 10°C min^{-1} in nitrogen atmosphere.

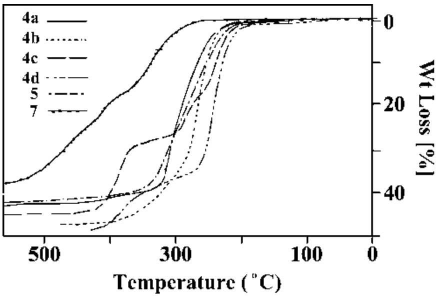


Figure 3. TGA of **4**, **5**, and **7** measured with a heating rate of 10 °C min^{-1} in argon atmosphere.

3. Conclusions

The reaction of 1-AAQ or 2-AAQ with aroyl isothiocyanates in ILs leads to an efficient synthesis of N-substituted N'-aroylthioureas, containing 9,10-anthraquinone moieties. The nature of the ILs, influences the reaction yield. All the dyes were characterized by ^{1}H- and ^{13}C NMR, IR, and UV–vis spectra and TG measurements. Some structural and physical properties of these dyes are reported.

4. Experimental

4.1. *General*

Compounds **1–3** were obtained from Fluka and were used without further purification. Melting point: Electrothermal-9100 apparatus; IR spectra: Shimadzu IR-460 spectrometer; ^{1}H- and ^{13}C NMR spectra: Bruker DRX-500 AVANCE instrument, in DMSO-d_6 at 500.1, 125.8, respectively, δ in ppm, J in Hz; EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in m/z. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. UV spectra were taken on a Shimadzu UV-160A spectrometer. Aroyl isothiocyanates **1** and **6** were prepared by a known procedure (*19*). All ILs were prepared and purified in accordance with the procedure described previously (*20*).

4.2. *General procedure for the preparation of 4 and 5*

The aroyl isothiocyanate (2 mmol) was added to a solution of the AAQ (2 mmol) in [bbim][Br] (2 g), and the solution was heated at 60 °C for 4–5 h (see Table 1). The reaction mixture was cooled to ambient temperature before work-up. The products were extracted with EtOAc (2 mL × 10 mL). The solvent was evaporated under reduced pressure to leave the crude product, which was purified by recrystallization from a 1:1 mixture of MeOH and EtOAc. The IL was recovered by addition of water (5 mL), then collected and dried under vacuum. These reactions were performed without any protective atmosphere of inert gas.

4.2.1. *1-Benzoyl-3-(9,10-dioxo-9,10-dihydro-anthracen-1-yl)thiourea (**4a**)*

Yellow powder, yield: 0.73 g (95%). m.p. 213–215 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1153 (C=S), 1577 (C=O), 1660 (C=O), 3400 (N–H). ^{1}H NMR (500 MHz, DMSO-d_6): 7.57 (2H, t, $J = 7.3$ Hz, CH), 7.67 (1H, t, $J = 7.3$ Hz, CH), 7.90–7.92 (3H, m, CH), 8.03–7.05 (2H, d, $J = 8.0$ Hz, CH), 8.14 (1H, d, $J = 7.7$ Hz, CH), 8.17 (2H, t, $J = 3.6$ Hz, CH), 8.71 (1H, d, $J = 8.0$ Hz, CH), 11.71 (1H, s, NH), 13.84 (1H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): 123.9 (CH), 125.0 (CH), 126.3 (CH), 126.8 (CH), 127.0 (CH), 128.3 (CH), 128.7 (CH), 132.0 (CH), 132.2 (CH), 132.8 (CH), 133.0 (CH), 133.7 (CH), 134.5 (N−C), 138.6 (C), 167.2 (C=O) 180.0, 181.8 (2C=O), 183.8 (C=S).

4.2.2. *1-(9,10-Dioxo-9,10-dihydro-anthracen-1-yl)-3-(4-methyl-benzoyl)thiourea (**4b**)*

Yellow powder, yield: 0.68 g (89%). m.p. 229–232 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1159 (C=S), 1577 (C=O), 1667 (C=O), 3425 (N−H). ^{1}H NMR (500 MHz, DMSO-d_6): 2.30 (3H, s, CH_3), 7.17 (2H, d, $J = 10.0$ Hz, CH), 7.20–7.22 (1H, m, CH), 7.27 (2H, d, $J = 10.0$ Hz, CH), 7.37–7.38 (3H, m, CH), 7.50–7.51 (1H, t, $J = 8.0$ Hz, CH), 8.70 (1H, d, $J = 8.0$ Hz, CH), 8.80–8.84 (1H, m, CH), 11.61 (1H, s, NH), 13.85 (1H, s, NH).

4.2.3. *1-(4-Bromobenzoyl)-3-(9,10-dioxo-9,10-dihydro-anthracen-1-yl)thiourea (4c)*

Red-orange solid, yield: 0.71 g (76%). m.p. 195–197 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1147 (C=S), 1574 (C=O), 1665 (C=O), 3468 (N−H). ^{1}H NMR (500 MHz, DMSO-d_6): 6.97 (2H, d, $J = 8.3$ Hz, CH), 7.47 (1H, t, $J = 7.5$ Hz, CH), 7.79–7.80 (3H, m, CH), 8.0 (2H, m, CH), 8.89 (1H, d, $J = 8.3$ Hz, CH), 8.29 (1H, dd, $J = 8.0$ Hz, $J = 4.0$ Hz, CH), 8.94 (1H, d, $J = 7.5$ Hz, CH), 9.20 (1H, s, NH), 14.25 (1H, s, NH).

4.2.4. *1-(4-Chlorobenzoyl)-3-(9,10-dioxo-9,10-dihydro-anthracen-1-yl)thiourea (**4d**)*

Red-orange solid, yield: 0.78 g (93%). m.p. 210–212 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1173 (C=S), 1577 (C=O), 1667 (C=O), 3418 (N−H). ^{1}H NMR (500 MHz, DMSO-d_6): 7.56 (2H, m, CH), 7.67 (1H, t, $J = 7.0$ Hz, CH), 7.91–7.92 (3H, m, CH), 8.0 (1H, d, $J = 4.5$ Hz, CH), 8.07 (2H, d, $J = 4.5$ Hz, CH), 8.18 (1H, t, $J = 4.5$ Hz, CH), 8.25 (1H, d, $J = 7.8$ Hz, CH), 9.08 (1H, d, $J = 7.5$ Hz, CH), 11.10 (1H, s, NH). 13.32 (1H, s, NH).

4.2.5. *5-Benzoyl-3-(9,10-dioxo-9,10-dihydro-anthracen-2-yl)thiourea (**5**)*

Red-brown solid, yield: 0.64 g (83%). m.p. 230–232 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1185 (C=S), 1574 (C=O), 1675 (C=O), 3200 (N−H). ^{1}H NMR (500 MHz, DMSO-d_6): 6.93 (1H, dd, $^3J = 8.2$ Hz, $^4J = 2.6$ Hz, CH), 7.20 (1H, d, $^4J = 2.3$ Hz, CH), 7.50 (2H, t, $J = 7.5$ Hz, CH), 7.65 (2H, t, $J = 7.2$ Hz, CH), 7.78 (2H, m, CH), 8.00 (3H, t, $J = 8.0$ Hz, CH), 7.94 (1H, d, $J = 8.5$ Hz, CH), 11.72 (1H, s, NH), 12.90 (1H, s, NH). ^{13}C NMR (125.7 MHz, DMSO-d_6): 121.0 (CH), 126.2 (CH), 126.3 (CH), 126.6 (CH), 127.7 (CH), 128.4 (CH), 128.7 (CH), 132.0 (CH), 132.2 (CH), 132.9 (CH), 133.0 (CH), 133.7 (CH), 134.8 (N−C), 143.3 (C), 167.9 (C=O) 180.0, 181.8 (2C=O), 183.3 (C=S).

4.3. *General procedure for the preparation of 7 and 8*

Terephthaloyl isothiocyanate (1 mmol) was added to a solution of the AAQ (2 mmol) in [bbim][Br] (3 g), and the solution was heated at 60 °C for 4–5 h (see Table 1). The reaction mixture was cooled to ambient temperature before work-up. The products were extracted with EtOAc (10 mL). The solvent was evaporated under reduced pressure to leave the crude product, which was purified by recrystallization from a 1:1 mixture of MeOH and EtOAc. The IL was recovered by addition of water (7 mL), then collected and dried under vacuum. These reactions were performed without any protective atmosphere of inert gas.

4.3.1. *N-(9,10-Dioxo-9,10-dihydro-1-anthracenyl) N′ -{4({[(9,10-dioxo-9,10-dihydro-1-anthracenyl)amino]carbothioy}aminocarbonyl)benzoyl}thiourea (**7**)*

Green powder, yield: 1.12 g (81%). m.p. 280–283 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1154 (C=S), 1577 (C=O), 1659 (C=O), 1686 (C=O), 3418 (N−H).

4.3.2. *N-(9,10-Dioxo-9,10-dihydro-2-anthracenyl)-N′-{4({[(9,10-dioxo-9,10-dihydro-2-anthracenyl)amino]carbothioy}aminocarbonyl)benzoyl}thiourea (**8**)*

Shiny green powder, yield: 1.16 g (84%). m.p. 285–288 °C. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1161 (C=S), 1188 (C=S), 1655 (C=O), 1628 (C=O), 1599 (C=O), 3268 (N−H), 3415 (N−H). ^{1}H NMR (500 MHz, DMSO-d_6): 7.71–7.85 (4H, m, 4CH), 8.00 (4H, s, 4CH), 8.04–8.25 (8H, m, 8CH), 8.74 (2H, s, CH), 11.95 (2H, s, 2NH), 12.76 (2H, s, 2NH).

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