Reaction of a *N*-anthrylcarbonylthiourea derivative with Cu^{2+} or H^+: unusual rearrangement to a highly fluorescent *S*-(9-anthryl)-isothiouronium salt

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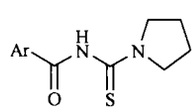
For the fluorescent ligand 1-(9-anthrylcarbonyl)-3,3-tetramethylenethiourea with $Cu(ClO_4)_2$ or strong acids an unusual rearrangement reaction occurred yielding a highly emissive *S*-(9-anthryl)isothiouronium salt. This rearrangement product was characterised by NMR spectroscopy and X-ray analysis as well as absorption and fluorescence spectroscopy. Additionally, the chemical and complexation behaviour of the *N*-anthrylcarbonyl-thiourea derivative is compared to that of its naphthyl and phenyl analogues.

Introduction

Substituted *N*-acylthioureas are well known as chelating agents for heavy, transition, and noble metal ions and their pH dependent complexation properties have been intensively investigated.[1–3] With these metal ions, *N*-benzoylthioureas for instance form strong neutral bidentate complexes (*cis* conformation preferred) with a six-membered ring chelate structure, the complex stoichiometry generally being 1:2 (M:L, with M = metal ion and L = ligand). A first example of *cis* and *trans* chelation has only recently been reported for a naphthoylthiourea derivative and Pt^{2+}.[4] In metal ion analysis, substituted *N*-acylthioureas have frequently been employed as complexing agents for the extraction of these cations and their trace enrichment *via* selective adsorption in combination with other analytical detection methods such as AAS or liquid chromatography (HPTLC and HPLC with UV detection).[5,6] They were also incorporated as cation specific receptors into pyrene and anthracene based modular fluorescent sensor molecules for heavy and transition metal ions[7–11] which are among the very few examples of such compounds showing chelation enhanced fluorescence (CHEF) with commonly known fluorescence quenchers as for instance paramagnetic Cu^{2+} or the heavy metal ion Hg^{2+}.[12–20] However, the structures of the cation complexes of the reported *N*-acylthioureas, *N*,*N*-diethyl-*N*′-pyren-1-ylcarbonylthiourea, *N*,*N*-diethyl-*N*′-4-(pyren-1-yl)butylthiourea, and *N*-methyl-*N*-(9-anthrylmethyl)-*N*′-benzoylthiourea, have not been presented yet.[7,8,11]

A previous study of the absorption and fluorescence properties of 1-(9-anthrylcarbonyl)-3,3-tetramethylenethiourea **1**, designed as a cation complexing fluoroionophore, was presented and its interaction with Cu^{2+} and Hg^{2+} as well as Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, and Ca^{2+} in acetonitrile was described.[9,10] Here, only addition of Cu^{2+} or Hg^{2+} to weakly fluorescent **1** led to measurable spectroscopic changes, the most intriguing effects being the appearance of a very intense emission band with a strongly increased fluorescence lifetime. In agreement with similar systems reported, we attributed these effects to complexation of **1** to Cu^{2+} and Hg^{2+}, *i.e.* to chelation induced blocking of a fluorescence quenching channel.[21–23] However, our spectroscopic data have not enabled us so far to give a comprehensive explanation of the complexation behaviour of **1** as well as its cation selectivity and the chemical structure of the highly fluorescent product formed with Cu^{2+} or Hg^{2+}.

For the design of new cation complexing fluoroionophores for heavy and transition metal ions, a better understanding of the actual binding sites and conformation of the cation complexes of fluorescent sensor molecules undergoing CHEF with these metal ions is highly desirable. This encouraged us to perform a detailed investigation of the interaction of compound **1** with Cu^{2+}, Hg^{2+}, Zn^{2+}, Ca^{2+}, and protons in acetonitrile employing NMR spectroscopy (^1H; ^{13}C), X-ray analysis as well as absorption and fluorescence spectroscopy and compare it to that of its naphthyl and phenyl derivatives **2** and **3**, respectively.



1-3

Ar = 9-anthryl (**1**), 1-naphthyl (**2**), phenyl (**3**)

Results and discussion

The *N*-anthrylcarbonylthiourea derivative **1**, its naphthyl analogue **2**, and its phenyl analogue **3** were obtained from the corresponding acyl isothiocyanates and pyrrolidine.[1]

Reaction of compound 1 with $Cu(ClO_4)_2$

For a detailed characterisation of the product formed upon addition of $Cu(ClO_4)_2$ to compound **1** in acetonitrile, *i.e.* the solvent used for the fluorometric investigations, different attempts to obtain crystals of the expected complex were performed in acetonitrile as well as methanol and THF, the latter solvent being best suited for crystal formation. To our astonishment, X-ray analysis of this species reveals the formation of a new compound, the *S*-(9-anthryl)-*N*,*N*-tetramethyleneisothiouronium perchlorate **8** instead of the expected Cu^{2+} complex of **1**. As will be discussed later, the absorption and

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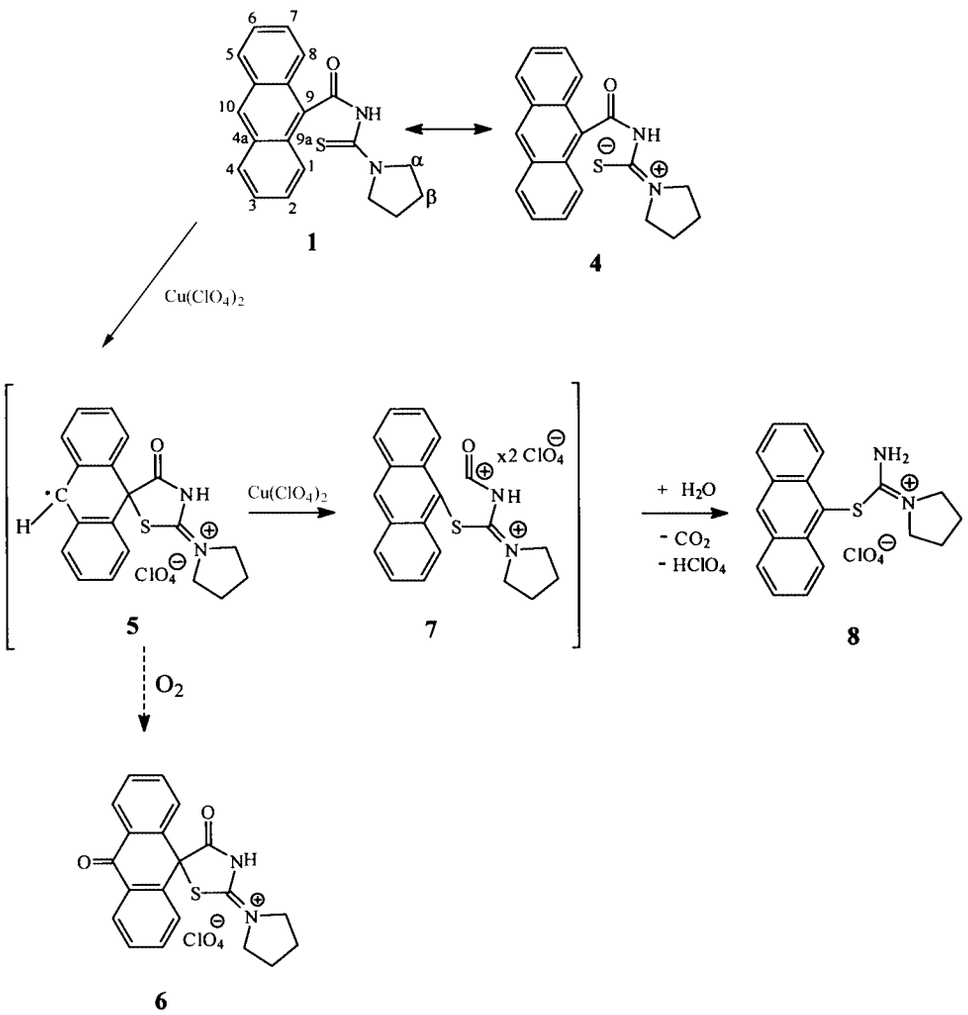


Scheme 1

fluorescence properties of this new anthracene derivative **8** in acetonitrile are identical to those previously reported by us for the assumed Cu^{2+} complex in this solvent.[9,10] Thus, the compound responsible for the observed fluorescence enhancement in the presence of $Cu(ClO_4)_2$ is obviously not a cation complex of **1** but the rearrangement product **8**, *i.e.* **1** does not act as a cation complexing fluorescent sensor molecule but as a fluorescent chemodosimeter[24,25] for Cu^{2+} in acetonitrile.

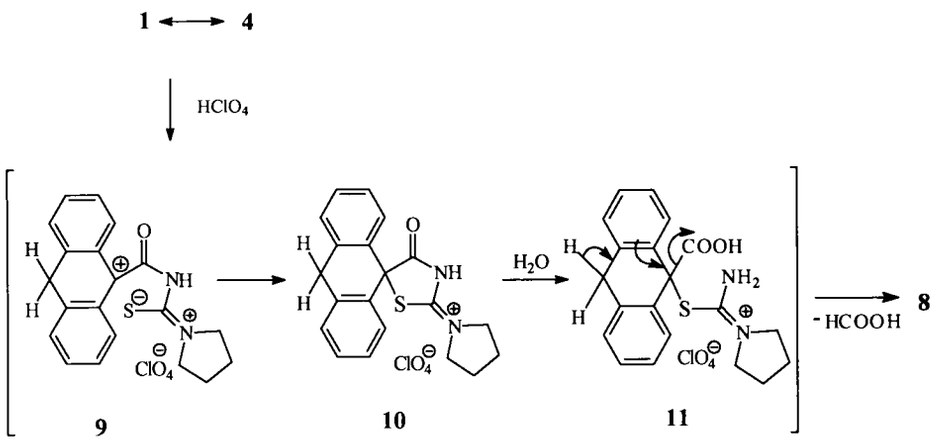
As the reaction proceeds in the presence of Cu^{2+}, the redox potential of the Cu^{2+}/Cu^{+} redox couple in acetonitrile being $E_{1/2} = +0.96$ V (*vs.* SCE),[26] the observed rearrangement of compound **1** upon addition of paramagnetic Cu^{2+} is very likely the result of a redox process in this solvent yielding **8** and diamagnetic Cu^{+}. The formation of Cu^{+} follows both from a colour test[27,28],† as well as from ^{1}H NMR measurements. Here, addition of up to two equivalents of $Cu(ClO_4)_2$ does not yield any significant broadening of the NMR signals as would be expected for a paramagnetic species such as Cu^{2+} being present. In accordance with these observations, we also found the yield of the product to be dependent on the molar ratio of Cu^{2+} to **1**, the highest yield of **8** being obtained for a ratio of 2:1, thus supporting a two step oxidative mechanism for the rearrangement observed.

As shown in Scheme 1, we propose as the initiation step the oxidation of the most reactive positions of the anthracene nucleus, *i.e.* C-9 and C-10, respectively. As a result of this oxidation, the *N*-anthrylcarbonylthiourea derivative is converted into the spiro intermediate **5** which already contains the bond between C-9 of the anthracene nucleus and the sulfur atom of the final product **8**. The second oxidation step leads to rearomatisation of the anthracene nucleus *via* an intermediate such as **7**, followed by hydrolysis and stabilisation yielding isolated **8**. This oxidative rearrangement mechanism requires the formation of a new C–S bond as the key step. A derivative of the proposed spiro intermediate **5**, **6**, could indeed be obtained by additional investigations, *i.e.* upon reaction of **1** with $Cu(ClO_4)_2$ in methanol, and was identified by X-ray analysis (see following paragraph).

In acetonitrile and THF, compound **1** is not stable under acidic conditions. In these solvents, treatment of **1** with either $HClO_4$ (30%) or tetrafluoroboronic acid (50%) yields **8** even without any oxidising reagent. The proposed mechanism for this protonation induced rearrangement is summarised in Scheme 2. Here, we expect protonation of the anthracene nucleus at C-10 to be the first step of the rearrangement reaction. Formation of **8** could then proceed *via* nucleophilic attack by sulfur at the positively charged C-9 position of **9**. Ring opening of the resulting spiro intermediate **10** by hydrolysis and rearomatisation of the intermediate **11** seems to be plausible. Thus, for **1**, either under oxidising or acidic conditions, the same rearrangement product **8** is isolated. To the best of our knowledge **8** is the very first aryl analogue of the *S*-alkylpseudothioureas known as potential antitumor drugs.[29]

In order to study the effect of the aryl substituent on this rearrangement, a similar investigation was performed with compound **2**. Addition of $Cu(ClO_4)_2$ to **2** under identical conditions as used for **1** does not lead to changes in the molecular structure of **2**. Obviously, the anthracene substituent is neces-

† Cu^{+} forms a crimson red complex with 2,2′-biquinoline with an intense absorption band at 549 nm whose detection is not interfered with by Cu^{2+}.



Scheme 2

sary to initiate the rearrangement reaction by formation of a radical (see **5**, Scheme 1). Most likely, this is the reason why for thioureas with their well investigated complexation behaviour the occurrence of such a rearrangement has not been described so far. Furthermore, in the case of other fluoroionophores containing both the fluorophore anthracene and an *N*-acylthiourea receptor, anthracene was always covalently linked (at its 9-position) to the receptor's N atom instead of being attached to its carbonyl group.[7,11]

X-Ray analysis

X-Ray analyses were performed with the starting material **1**, spiro compound **6**, and the isolated product of the rearrangement reaction **8**. The resulting molecular structures including the numbering scheme adopted are presented in Fig. 1.

Compound **1** crystallises in the triclinic space group $P\bar{1}$ (no. 2) with two symmetry independent molecules A and B of which only A is depicted in Fig. 1(a). Both molecules have the same configuration but slightly different conformations. The largest difference of the corresponding torsion angles defining the conformation of the molecule is observed for C(20)–C(7)–C(6)–N(2). This angle rises to 109.4 and 102.6° in molecules A and B, respectively. Both molecules are linked *via* two intermolecular hydrogen bonds, *i.e.* N(2A)–H···S(1B) 3.466(4) and N(2B)–H···S(1A) 3.424(4) Å, forming dimers in the crystalline state. The average bond distances N(1)–C(5) 1.308(5) and C(5)–S(1) 1.670(4) Å suggest that the starting compound can be described as a mesomeric structure of **1** and **4**, respectively.

For compound **6** (Fig. 1b) both five-membered rings are nearly coplanar. The torsion angle N(2)–C(5)–N(1)–C(1) rises to 0.0(7)°. This value and the short bond distances N(1)–C(5) 1.302(7), C(5)–N(2) 1.308(8), N(2)–C(6) 1.349(7) Å, and C(6)–O(1) 1.203(7) Å suggest a strong delocalisation of the π-electrons between N(1) and O(1).

X-Ray analysis of compound **8** (Fig. 1c) confirms the chemical structure of the reaction product illustrated in Schemes 1 and 2, respectively. The short bond distances C(5)–N(1) 1.312(5) Å and C(5)–N(2) 1.345(6) Å show that the positive charge of the *S*-(9-anthryl)-*N*,*N*-tetramethyleneisothiouronium cation is distributed between these three atoms. There is a hydrogen bond between the amino group of the cation and a perchlorate oxygen atom, the distance between N(2) and O(1) being 2.840(8) Å.

NMR spectroscopy

For a better understanding of the interaction of the *N*-aroylthioureas **1**–**3** with diamagnetic metal ions in acetonitrile, ^{1}H and ^{13}C NMR measurements were performed with solutions of ligands **1** and **3** in CD_3CN in the presence of metal perchlorates, employing M : L concentration ratios of 10 : 1 for Ca^{2+}, 3 : 1 for Zn^{2+}, and 3 : 1 for Hg^{2+}, respectively. The aim of this NMR investigation was (i) to study the solution of **1** after addition of $Hg(ClO_4)_2$ also yielding a strongly fluorescent product, (ii) to determine whether the *N*-benzoylthiourea derivative **3** undergoes either complexation or a chemical reaction with Hg^{2+} and (iii) to show whether ligand complexation occurs at least for **1** and **3** with Zn^{2+}. Furthermore, as a blind experiment, NMR measurements with Ca^{2+} which should not be bound by *N*-acylthiourea derivatives were performed.

Table 1 Metal ion induced changes in chemical shift $\Delta\delta$

Ligand	Metal ion	M : L[a]	$\Delta\delta$
1	Ca^{2+}	10 : 1	0.04[b]; 0.37[c]
1	Zn^{2+}	3 : 1	0.05[b]; 0.33[c]
1	Hg^{2+}	3 : 1	0.35[b]; 5.77[c]
3	Ca^{2+}	10 : 1	0.02[d]; 0.24[e]
3	Zn^{2+}	4 : 1	0.12[d]; 1.60[e]
3	Hg^{2+}	3 : 1	0.11[d]; 1.73[e]

[a] Metal ion (M) to ligand (L) concentration ratio. [b] $\Delta\delta$ (H-10). [c] $\Delta\delta$ (C-10). [d] $\Delta\delta$ (H-4). [e] $\Delta\delta$ (C-4).

A direct measure for the interaction of these three metal ions with compounds **1** and **3** follows from the cation induced changes in chemical shift of H-10 and C-10 in the case of **1** as well as H-4 and C-4 in the case of **3**, see Table 1. For **3** and the metal ions Zn^{2+} and Hg^{2+}, the observed cation induced changes in chemical shift which clearly exceed those occurring with Ca^{2+} are ascribed to formation of a cation complex in agreement with the complexation behaviour reported for other *N*-acylthiourea derivatives.[2] In the case of **1** and Zn^{2+}, the size of the cation induced effect is very similar to that noticed for Ca^{2+}. However, analogously to other *N*-acylthiourea derivatives and **3**, complexation of Zn^{2+} to **1** may still occur. For **1** and Hg^{2+}, a comparison between the ^{1}H and ^{13}C NMR spectra of the mixture of **1** and $Hg(ClO_4)_2$ and those obtained for **8** confirms the formation of the rearrangement product **8** in the presence of Hg^{2+}. Thus, in acetonitrile, **8** acts as a fluorescent chemodosimeter for Hg^{2+} as well.

Absorption and fluorescence spectroscopy

Absorption and fluorescence measurements were carried out in order to (i) confirm the identity of the spectral data previously published[9,10] with those obtained for the isolated rearrangement product **8** and (ii) estimate the general analytical applicability of compound **1**. The absorption and fluorescence properties of **1** and **8** in solvents of different polarity are in Table 2.

The anthracene-like absorption spectrum of compound **1** suggests a perpendicular orientation of the fluorophore and the carbonyl function of the cation receptor in the ground state.

Table 2 Spectroscopic data of compounds **1** and **8** in selected solvents

Compound	Solvent	λ_{max} (abs)/nm	λ_{max} (em)/nm	φ_f	τ_f/ns
1	Methanol	330, 346, 364, 382	443[a]	0.001	0.030
	Acetonitrile	331, 346, 364, 383	432[a]	0.002	0.037
	Dichloromethane	332[b], 349, 366, 386	456[a]	0.003	0.074
	1,4-Dioxane	332, 348, 366, 384	415[b], 435[a]	0.001	n.d.[c]
	Diethyl ether	329, 345, 363, 382	434[a]	0.002	n.d.
	Toluene	329[b], 345, 363, 382	443[a]	0.006	0.080
8	Acetonitrile	346, 363, 383, 402	418, 440, 465[b]	0.49	10.60
	Diethyl ether	346, 363, 383, 403	413, 436, 463	0.40	9.10

[a] Diffuse, not anthracene-like structured. [b] Shoulder. [c] Not determined.

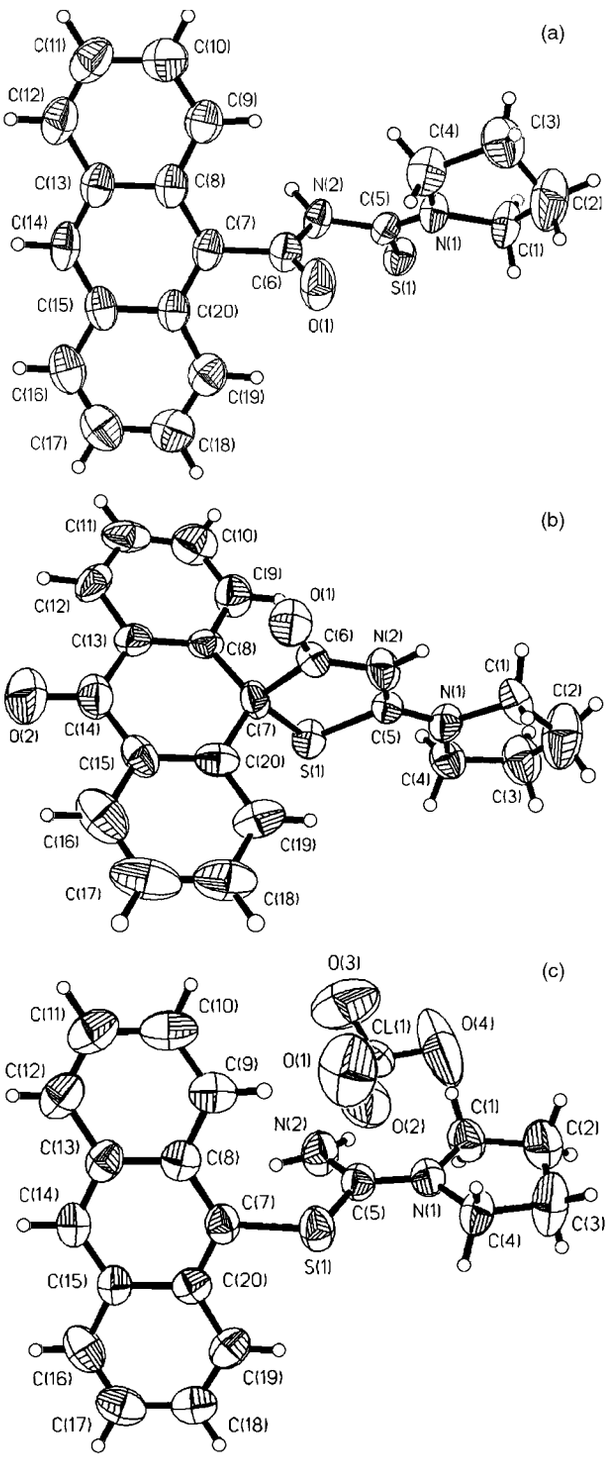


Fig. 1 Thermal ellipsoid (SHELXTL) drawings of compounds **1** (a), **6** (b) and **8** (c) with 50% probability of electron density enclosed. The crystal structure of **1** contains two symmetry independent molecules A and B of which only A is shown.

Its structureless emission is red shifted compared to that of anthracene in all the solvents employed. This is attributed to excited state rotation of the carbonyl group of the *N*-acylthiourea moiety of **1** into the plane of the anthracene π-system in accordance with the spectroscopic properties of other 9-carbonyl substituted anthracene derivatives.[30–32] More or less independent of solvent polarity, the fluorescence of **1** is very weak due to the 9-substituent, *i.e.* either the carbonyl group[32] or the *N*-acylthiourea moiety[8] acting as a fluorescence quencher. The fluorescence quantum yield of 9-substituted anthracene derivatives is often very low or negligible for ketones or aldehydes due to rapid intersystem crossing from $S_{1\pi\pi^*}$ to energetically low lying triplet states ($T_{n\pi^*}$) whereas carboxylic acids, esters or amides show a moderate to strong emission. In the latter compounds, the electron donating substituents shift the nπ* level to higher energies thus making the intersystem crossing process less efficient.[32]

Both the absorption and emission spectrum of compound **8** are in good agreement with the data previously reported by us for the assumed Cu^{2+} complex of **1**.[9,10] Obviously, complete conversion of the *N*-anthrylcarbonylthiourea derivative **1** into **8** occurs at a concentration ratio of 1:2 for **1** and Cu^{2+}. The bathochromic and hypsochromic shift of the low energy absorption band of **8** compared to **1** both point to electronic interaction between the anthracene π-system and the sulfur orbitals of the isothiouronium group already in the ground state of the molecule.[33] We tentatively assume the latter. As is typical for 9-substituted anthracene derivatives, the 9-substituent has a stronger influence on the spectral features of the fluorescence spectrum than the absorption spectrum. Furthermore, fluorescence quenching due to the 9-substituent of **1** does not occur for **8** resulting in this fluorescent chemodosimeter type behaviour[24,25] in acetonitrile.

Conclusion

Here, we could show that the main product of the reaction of the *N*-anthrylcarbonylthiourea derivative **1** with $Cu(ClO_4)_2$ or $Hg(ClO_4)_2$ in acetonitrile is not a cation complex but strongly fluorescent *S*-(9-anthryl)-*N*,*N*-tetramethyleneisothiouronium perchlorate **8**. This species could be also obtained upon addition of a strong acid such as $HClO_4$ or tetrafluoroboronic acid to **1** in acetonitrile as well as THF. Thus, with this oxidative or protonation induced rearrangement, the very first *S*-arylpseudothiourea derivative could be synthesized.

Experimental

General methods

The purity of the synthesized compounds was checked by reversed phase HPLC (HPLC set up from Merck-Hitachi; RP18 column; acetonitrile–water 75:25 (v/v) as eluent) employing UV detection (UV detector from Knaur; wavelength fixed at 310 nm). The melting points measured with a digital melting point analyser IA 9100 (Kleinfeld GmbH) are uncorrected.

Materials for the synthesis and spectroscopy

The starting materials for the synthesis were obtained from Aldrich. The solvents were purchased from Aldrich and Fluka and were of spectroscopic grade. Bidistilled water (pH 6.39) was provided by the Laboratory for Trace Elemental Analysis, BAM, Berlin. The metal perchlorates purchased from ALFA were of the highest purity commercially available and dried prior to use. All the spectroscopic experiments were carried out in air saturated solutions.

Absorption and fluorescence spectroscopy

Steady state measurements were performed on a SPECORD M400/M500 absorption spectrometer from Carl Zeiss Jena and a Perkin-Elmer LS50B fluorometer, respectively. For the determination of the relative fluorescence quantum yields (φ_f), the optical densities (od) of the solutions at the excitation wavelength were adjusted to 0.1 ± 0.001 in 100 mm absorption cells. These solutions were then transferred to a 10 mm fluorescence quartz cell and the fluorescence measurements were carried out with a 90° standard geometry. Anthracene in air-saturated ethanol ($\varphi_f = 0.20$) and quinine sulfate ($\varphi_f = 0.55$) in 0.5 M H_2SO_4 were used as fluorescence standards.[34,35]

Time-resolved fluorescence measurements were performed with a laser impulse fluorometer with ps time resolution (ps-LIF) described elsewhere.[10] The second harmonic output of a regenerative mode-locked Ti:Sapphire laser (Spectra Physics Model 350) at a repetition rate of either 82 or 4 MHz was used to excite the sample and the fluorescence was collected at right angles (emission monochromator with a spectral bandwidth of 8 nm). The temporal response of the ps-LIF was typically 33 ps. The fluorescence decay curves were recorded with a time-correlated single photon counting set up and a time division of 5.2 (82 MHz version) or 52.6 ps per channel (4 MHz version), typical count rates of $(2–4) \times 10^3$ counts per second, and for a single decay data were accumulated up to 20 000 counts in the peak channel. The temporal calibration of the experimental set up was checked with rose bengal in methanol ($\tau_f = 0.50 \pm 0.02$ ns[34] with τ_f = fluorescence lifetime), 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) in ethanol ($\tau_f = 1.35 \pm 0.20$ ns[35]), and fluorescein 27 in 0.1 M NaOH ($\tau_f = 4.50 \pm 0.03$ ns[35]). For the analysis of the fluorescence decay data, the software package IBH Decay Analysis Software V4 (IBH Consultants Ltd.) was employed.

X-Ray analysis

X-Ray data collection of compounds **1** and **6** was carried out on an Enraf-Nonius CAD-4 diffractometer at 293 K using Mo-Kα radiation ($\lambda = 0.71073$ nm) monochromatized by a graphite crystal. Data were collected employing the $2\theta–\omega$ scan technique in the range $3.0 < 2\theta < 44°$. Both structures were solved by direct methods and refined by full-matrix least-squares calculations (MOLEN, Enraf Nonius, Delft, Netherlands, 1992). Data for **8** were collected in the range $3.4 < 2\theta < 46.4°$ on a Bruker AXS SMART diffractometer under similar conditions as described for **1** and **6**. Structure solution using direct methods and full-matrix least-squares refinement were performed with SHELXTL, G. Sheldrick, University of Göttingen, Germany, 1977.

Crystal data of compound 1. Colourless prismatic crystal with dimensions $0.56 \times 0.18 \times 0.06$ mm. Triclinic, space group $P\bar{1}$ (no. 2), $a = 9.978(3)$, $b = 11.179(4)$, $c = 16.066(10)$ Å, $\alpha = 105.24(4)$, $\beta = 98.10(4)$, $\gamma = 94.86(2)$, $V = 1697.8(13)$ Å^3, $Z = 4$, $D_c = 1.308$ Mg m^{-3}, $\mu = 0.199$ mm^{-1}, and $M = 334.42$ for $C_{20}H_{18}N_2OS$. Total number of reflections 4448, 4146 independent [$R_i = 0.0277$], 2831 observed [$I > 2.0\sigma(I)$]. Number of refined parameters 434. Final $R1$ (on F) = 0.049, $wR2$ (on F^2) = 0.1267.

Crystal data of compound 6. Light-yellow prismatic crystal with dimensions $0.55 \times 0.15 \times 0.10$ mm. Monoclinic, space group $P2_1/c$, $a = 10.029(3)$, $b = 10.546(11)$, $c = 15.338(10)$ Å, $\beta = 94.02(4)°$, $V = 1618(2)$ Å^3, $Z = 4$, $D_c = 1.434$ Mg m^{-3}, $\mu = 0.217$ mm^{-1}, and $M = 349.43$ for $C_{20}H_{17}N_2O_2S$. Total number of reflections 2210, 1927 independent [$R_i = 0.052$], 1052 observed [$I > 2.0\sigma(I)$]. Number of refined parameters 227. Final $R1$ (on F) = 0.068, $wR2$ (on F^2) = 0.1473.

Crystal data of compound 8. Light-yellow crystal, needle shaped, with dimensions $0.60 \times 0.11 \times 0.08$ mm. Orthorhombic, space group $P2_12_12_1$, $a = 6.1895(1)$, $b = 12.7169(2)$, $c = 23.8077(2)$ Å, $V = 1873.93(5)$ Å^3, $Z = 4$, $D_c = 1.442$ Mg m^{-3}, $\mu = 0.344$ mm^{-1}, and $M = 406.87$ for $C_{19}H_{19}N_2O_4ClS$. Total number of reflections 8028, 2671 independent [$R_i = 0.044$], 2497 observed [$I > 2.0\sigma(I)$]. Number of refined parameters 253. Final $R1$ (on F) = 0.057, $wR2$ (on F^2) = 0.177.

CCDC reference number 188/238. See http://www.rsc.org/suppdata/p2/b0/b000138o/ for crystallographic files in .cif format.

NMR spectroscopy

^{1}H and ^{13}C NMR spectra of compounds **1**, **2**, **3**, and **8** (0.005–0.01 M in CD_3CN) were recorded on a Bruker DMX 400 spectrometer at 400 and 100 MHz, respectively. For the NMR experiments with Ca^{2+}, Zn^{2+}, and Hg^{2+}, solutions of the corresponding metal perchlorates were added to a previously measured solution of **1** or **3** (M : L concentration ratio of 10 : 1 for Ca^{2+}, 3 : 1 for Zn^{2+}, and 3 : 1 for Hg^{2+}, respectively, see Table 1). Chemical shifts were referenced to tetramethylsilane using solvent signals. The 2-D spectra were acquired employing software from Bruker. For **1**, ^{1}H–^{1}H COSY spectra (including long range variants) as well as hetero correlated ^{13}C–^{1}H spectra were measured in order to match the ^{1}H signals with the corresponding ^{13}C NMR spectra and signals of the quaternary carbon atoms were matched employing long range measurements of the ^{13}C–^{1}H hetero correlation.

The assignment of the ^{1}H doublets to H-1 and H-4 in compound **1** was based on the observation of the long range coupling constant ^5J(H-1, H-10) of *ca.* 1 Hz in the COSY spectra. The same coupling constant ^5J(H-4, H-8) was used for the assignment of the doublet signals of H-4 and H-8 of the naphthyl derivative **2**.[36,37] The other coupling constants of the aromatic systems were in agreement with commonly observed values (for **2**: ^3J(H-2, H-3) = 7.0, ^3J(H-3, H-4) = 8.4, ^4J(H,H) = 1.4 Hz).[36,37]

Preparations

1-(9-Anthrylcarbonyl)-3,3-tetramethylenethiourea (1). Anthracene-9-carboxylic acid (2.22 g, 1×10^{-2} mol) was converted into the acid chloride following a literature procedure.[38] To the stirred solution of the crude acid chloride in 20 ml of acetone, a solution of NH_4SCN (0.78 g, 1×10^{-2} mol) in acetone (10 ml) was added slowly at room temperature. After stirring for 30 min, pyrrolidine (1.29 ml, 1.5×10^{-2} mol) was added and stirring was continued for 15 min. The reaction mixture was diluted with dilute HCl (100 ml, 2%). The crude solid product was isolated by filtration and recrystallised twice from Pr^{i}OH. Yield 1.6 g, 48%, mp 195–196 °C (Found: C, 71.38; H, 5.40; N, 8.33. Calc. for $C_{20}H_{18}N_2OS$: C, 71.82; H, 5.42; N, 8.37%). ^{1}H NMR (CD_3CN): δ 2.07–2.13 (m, 4H, H-β), 3.82 (t, 2H, H-α′), 4.05 (t, 2H, H-α), 7.53–7.63 (m, 4H, H-2, H-7, H-3, H-6), 8.08 (d, 2H, H-1, H-8), 8.11 (d, 2H, H-4, H-5), 8.65 (s, 1H, H-10), 9.11 (s, 1H, NH). ^{13}C NMR (CD_3CN): δ 25.34 (C-β), 26.88 (C-β′), 53.57 (C-α), 55.15 (C-α′), 125.57 (C-1), 126.76 (C-3), 128.18 (C-2), 129.01 (C-9a), 129.64 (C-4), 129.79 (C-10), 131.61 (C-9), 131.99 (C-4a), 167.09 (C=O), 176.87 (C=S).

1-(1-Naphthoyl)-3,3-tetramethylenethiourea (2). Compound **2** was prepared from its commercially available acid chloride

(0.95 g, 5×10^{-2} mol) following the same procedure as described for **1a**. Recrystallisation from nitromethane gave pure **2** as colourless crystals. Yield 0.78 g, 55%, mp 177–178 °C (Found: C, 67.22; H, 5.35; N, 9.81. Calc. for $C_{16}H_{16}N_2OS$: C, 67.58; H, 5.67; N, 9.85%). ^{1}H NMR (CD_3CN): δ 2.03 (m, 4H, H-β, H-β′), 3.81 (t, 2H, H-α′), 3.82 (t, 2H, H-α), 7.55 (dd, 1H, H-3), 7.60 (m, 2H, H-6, H-7), 7.78 (d, 1H, H-2), 7.97 (d, 1H, H-5), 8.09 (d, 1H, H-4), 8.33 (d, 1H, H-8), 8.95 (s, 1H, NH). ^{13}C NMR (CD_3CN): δ 25.36 (C-β′), 26.64 (C-β), 53.16 (C-α′), 55.05 (C-α), 125.76 (C-3), 126.04 (C-8), 127.59 (C-7), 127.79 (C-2), 128.41 (C-6), 129.46 (C-5), 131.15 (C-8a), 132.56 (C-4), 133.22 (C-1), 134.69 (C-4a), 166.69 (CO) and 177.43 (CS).

***S*-(9-Anthryl)-*N*,*N*-tetramethyleneisothiouronium perchlorate (8).** Compound **8** was prepared in two different ways, *i.e. via* reaction of **1** with $Cu(ClO_4)_2$ in THF (method A) or *via* reaction of **1** with $HClO_4$ or HBF_4 in THF or acetonitrile (method B).

Method A. A solution of compound **1** (0.334 g, 1×10^{-3} mol) in 5 ml of THF was added dropwise to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.74 g, 2×10^{-3} mol) in 5 ml of THF at room temperature and the mixture stirred for 14 h. The precipitated crystals were collected, washed with THF, and recrystallised from nitromethane to give pure **8** as light-yellow crystals. Yield 0.19 g, 46.6%, mp 298–300 °C; (Found: C, 56.09; H, 4.65; N, 6.83. Calc. for $C_{19}H_{18}ClN_2O_4S$: C, 56.22; H, 4.47; N, 6.90%). ^{1}H NMR (CD_3CN): δ 2.13 (m, 4H, H-β, H-β′), 3.51 (t, 2H, H-α′), 3.96 (t, 2H, H-α), 7.67 (m, 2H, H-3, H-6), 7.79 (m, 2H, H-2, H-7), 6.40 (very broad, 1H, NH), 8.25 (d, 2H, H-1, H-8), 8.60 (d, 2H, H-4, H-5), 8.99 (s, 1H, H-10). ^{13}C NMR (CD_3CN): δ 25.81 (C-β′), 26.26 (C-β), 51.58 (C-α), 52.02 (C-α′), 114.89 (C-9), 125.71 (C-1), 127.23 (C-3), 130.31 (C-2), 130.56 (C-4), 133.21 (C-9a), 135.56 (C-10), 136.43 (C-4a), 164.89 (CNS).

Method B. 1 ml of $HClO_4$ (30%) or HBF_4 (50%) was added to a solution of compound **1** (0.167 g, 5×10^{-4} mol) in acetonitrile (3 ml). The reaction mixture was stirred at room temperature overnight and cooled to 0 °C. The precipitated product **8** was isolated by filtration, washed with acetonitrile, and recrystallised from nitromethane. Yield 0.12 g (59%) for $HClO_4$ and 0.08 g (42%) for HBF_4, respectively.

1-[10-Oxo-9,10-dihydroanthracene-9-spiro-5′-(4′-oxo-1′,3′-thiazolidin-2′-ylidene)]pyrrolidinium perchlorate (6). A mixture of compound **1** (0.167 g, 5×10^{-4} mol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.185 g, 5×10^{-4} mol) in methanol (5 ml) was refluxed for 1 h. The hot reaction mixture was filtered and cooling led to the precipitation of light-yellow crystals. These crystals were identified as spiro compound **6** by X-ray analysis.

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References

1 L. Beyer, E. Hoyer, H. Hennig, R. Kirmse, H. Hartmann and J. Liebscher, *J. Prakt. Chem.*, 1975, **317**, 829.
2 P. Mühl, K. Gloe, F. Dietze, E. Hoyer and E. Beyer, *Z. Chem.*, 1986, **26**, 81.
3 K. H. König, H. J. Pletsch and M. Schuster, *Fresenius Z. Anal. Chem.*, 1986, **325**, 621.
4 R. Koch, J. du Toit, M. R. Caira and C. Sacht, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 785.
5 M. Schuster, *Nachr. Chem. Tech. Lab.*, 1992, **40**, 682.
6 M. Schuster, *Fresenius Z. Anal. Chem.*, 1992, **342**, 791.
7 M. Schuster and E. Unterreitmaier, *Fresenius J. Anal. Chem.*, 1993, **346**, 630.
8 E. Unterreitmaier and M. Schuster, *Anal. Chim. Acta*, 1995, **309**, 339.
9 U. Resch, K. Rurack, Y. L. Bricks and Y. L. Slominskii, *J. Fluoresc.*, 1997, **7**, 31S.
10 U. Resch and K. Rurack, *Proc. SPIE Int. Soc. Opt. Eng.*, 1997, **3105**, 96.
11 M. Sandor, F. Geistmann and M. Schuster, *Anal. Chim. Acta*, 1999, **388**, 19.
12 P. Ghosh, P. K. Bharadwaj, S. Mandal and S. Ghosh, *J. Am. Chem. Soc.*, 1996, **118**, 1553.
13 P. Ghosh, P. K. Bharadwaj, J. Roy and S. Ghosh, *J. Am. Chem. Soc.*, 1997, **119**, 11903.
14 R. Krämer, *Angew. Chem.*, 1998, **110**, 804.
15 K. Kubo, T. Sakurai and A. Mori, *Talanta*, 1999, **50**, 73.
16 K. Rurack, M. Kollmannsberger, U. Resch-Genger and J. Daub, *J. Am. Chem. Soc.*, accepted for publication.
17 K. Rurack, Y. L. Bricks, Y. L. Slominski and U. Resch, *Dyes Pigm.*, 1998, **36**, 121.
18 G. Hennrich, H. Sonnenschein and U. Resch-Genger, *J. Am. Chem. Soc.*, 1999, **121**, 5073.
19 B. Ramachandram and A. Samanta, *J. Phys. Chem. A*, 1998, **102**, 10579.
20 B. Ramachandram and A. Samanta, *Chem. Commun.*, 1997, 1537.
21 L. Fabbrizzi, G. Francese, M. Licchelli, P. Pallavicini, A. Perotti, A. Poggi, D. Sacchi and A. Taglietti, in *Chemosensors of Ion and Molecule Recognition*, ed. J. P. Desvergnes and A. W. Czarnik, Kluwer Academic, Dordrecht, 1997, p. 75.
22 F. Fages, J. P. Desvergnes, H. Bouas-Laurent, P. Marsau, J. M. Lehn, F. Kotzyba-Hibert, A. M. Albrect-Gary and M. Al-Joubbeh, *J. Am. Chem. Soc.*, 1989, **111**, 8672.
23 M. E. Huston, C. Engleman and A. W. Czarnik, *J. Am. Chem. Soc.*, 1990, **112**, 7054.
24 Y. Chae and A. W. Czarnik, *J. Am. Chem. Soc.*, 1992, **144**, 9704.
25 V. Dujols, F. Ford and A. W. Czarnik, *J. Am. Chem. Soc.*, 1997, **119**, 7386.
26 F. Farha, Jr. and R. T. Iwamoto, *J. Electroanal. Chem. Interfacial Electrochem.*, 1964, **8**, 56.
27 P. Smirnoff, *Helv. Chim. Acta*, 1921, **4**, 802.
28 G. A. Schwarzenbach, E. Kampitsch and R. Steiner, *Helv. Chim. Acta*, 1945, **28**, 828.
29 T. P. Wunz, R. T. Dorr, D. S. Alberts, C. L. Tunget, J. Einspahr, S. Milton and W. A. Remers, *J. Med. Chem.*, 1987, **30**, 1313.
30 C. Werner and D. M. Hercules, *J. Phys. Chem.*, 1969, **73**, 2005.
31 T. C. Werner and J. Rodgers, *J. Photochem.*, 1986, **32**, 59.
32 S. Hirayama, *J. Chem. Soc.*, *Faraday Trans. 1*, 1982, **78**, 2411.
33 S. Schoof, H. Güsten and C. von Sonntag, *Ber. Bunsen Ges. Phys. Chem.*, 1978, **82**, 1068.
34 D. F. Eaton, *J. Photochem. Photobiol. B*, 1988, **2**, 523.
35 R. A. Velapoldi and M. S. Epstein, *ACS Symp. Ser.*, 1989, **383**, 98.
36 E. Kleinpeter, S. Behrendt and L. Beyer, *Z. Anorg. Allg. Chem.*, 1982, **495**, 105.
37 E. Pretsch, T. Clerc, J. Seibl and W. Simon, in *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden*, 3rd edn., Springer, Berlin, 1990, pp. H245, H250.
38 E. Ciganek, *J. Org. Chem.*, 1980, **45**, 1497.