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# Synthesis, Properties, and X-ray Structure of 6-Aza-5,7,12,14-tetrathiapentacene as a Novel Polyheterocyclic Electron Donor, and Related Compounds

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Two new compounds, 1-aza-2,3-dichlorothianthrene (**5**) and 6-aza-5,7,12,14-tetrathiapentacene (**6**) have been prepared by reaction of 2,3,5,6-tetrachloropyridine (**4**) and 1,2-benzenedithiol in dimethylformamide (DMF) in the presence of sodium bicarbonate. On the other hand, the synthesis of two known compounds, 1-azathianthrene (**7**) and 5,7,12,14-tetrathiapentacene (**8**) have been improved by using the same synthetic procedure as above, starting from 2,3-dichloropyridine and 1,2,4,5-tetrachlorobenzene, respectively. The radical cations of **6**−**8** have been generated in fluid solution and they are stable enough to be analyzed by electron paramagnetic resonance (EPR). The hyperfine coupling (hfc) constants in the EPR spectra have been assigned according with those from thianthrene radical cation (**10**), reported in the literature, and with semiempirical estimations (McLachlan method). The cyclic voltammogram of **6** exhibits a redox couple ($E^\circ = 1.07$ V *vs* SCE) which is attributed to the oxidation to its radical cation $\mathbf{6}^{\bullet+}$, and a second irreversible peak ($E_p^a = 1.25$ V) which is ascribed to the formation of the unstable dication $\mathbf{6}^{2+}$. X-ray structure of **6** shows that the molecule has a stable chair-shaped conformation with an interplanar angle between benzenes and pyridine ring of 134.7(1)°. The crystal packing presents a stacking pattern and the molecules overlap showing diagonal shifts in the stack.

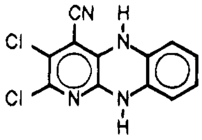
## Introduction

A great interest has been focused on the organic charge-transfer complexes with high electrical conductivity and in the chemistry of the donor and acceptor species.[2] One way to the development of the chemistry and physics of these charge-transfer complexes is to explore a new class of donors so as to extend the range of molecular conductors.

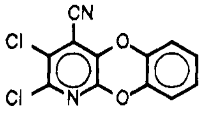
The incorporation of polarizable heteroatoms within the donor framework is regarded as one important aspect to design new donor molecules, as it could increase interchain interaction in the solid state and thus bring about the stable metallic state.

Our molecular design strategy for new organic electron donors comes from the study of nucleophilic displacements on the pentachloropyridine and 2,3,5,6-tetrachloropyridine.

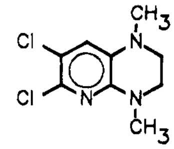
Pentachloropyridine readily undergoes nucleophilic substitution at the 2- and/or 4-position.[3] Large nucleophiles attack preferentially the less-hindered 2-position while small nucleophiles may react exclusively at the more activated 4-position.[3] In this context, the behavior of tetrachloro-4-cyanopyridine with bidentate reagents such as *o*-phenylendiamine and *o*-dihydroxybenzene was investigated, and new polycyclic heteroaromatic compounds **1** and **2** were obtained.[4]



**1**



**2**



**3**

More recently, the reaction of the easily available 2,3,5,6-tetrachloropyridine (**4**) with tetramethylethylenediamine gave 6,7-dichloro-1,4-dimethyl-2,3-dihydropyrido[2,3-*b*]pyrazine (**3**).[5] In all these reactions, the initial attack by the bidentate reagent occurs in the 2-position of the pyridine ring followed by intramolecular cyclization in the 3-position.[4]

Now we report the synthesis and physical properties of 1-aza-2,3-dichlorothianthrene (**5**) and 6-aza-5,7,12,14-tetrathiapentacene (**6**) by the reaction of 2,3,5,6-tetrachloropyridine with 1,2-benzenedithiol. Very few papers have appeared in the literature about 1-azathianthrene (**7**)[6] and 5,7,12,14-tetrathiapentacene (**8**);[7] we have im-

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[1] (a) CETS Institut Químic de Sarriá. (b) Unitat de Cristallografía. (c) Departament de Química Física. (d) Centre d'Investigació i Desenvolupament. (e) Departament d'Enginyeria Química.

[2] *Proceedings of the International Conference on Science and Technology of Synthetic Metals (ICSM'92)*, Göteborg, Sweden, 1992, published in *Synth. Methods* **1993**, *55–57*.

[3] Iddon, B.; Suchitzky, H. In *Polychloroaromatic Compounds*; H. Suchitzky, Ed., Plenum: London, 1974; Chap. 2; and references cited therein.

[4] Dainter, R. S.; Juliá, L.; Suschitzky, H.; Wakefield, B. J. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2897.

[5] Juliá, L.; Rius, J.; Suschitzky, H. *Heterocycles* **1992**, *34*, 1539.

[6] (a) Puig-Torres, S.; Martín, G. E. *J. Heterocycl. Chem.* **1982**, *19*, 1441. (b) Larson, S. B.; Simonsen, S. H.; Martín, G. E.; Smith, K.; Puig-Torres, S. *Acta Crystallogr.* **1984**, *C40*, 103.

[7] (a) Max Ziegler, V.; Roda, W. *Chem. Zeitung* **1976**, *100*, 195. (b) Nesterov, V. N.; Shklover, V. E.; Struchkov, Y. T.; Sergeev, V. A.; Nedel'kin, V. I.; Ivanova, I. S. *Acta Crystallogr.* **1986**, *42*, 720.

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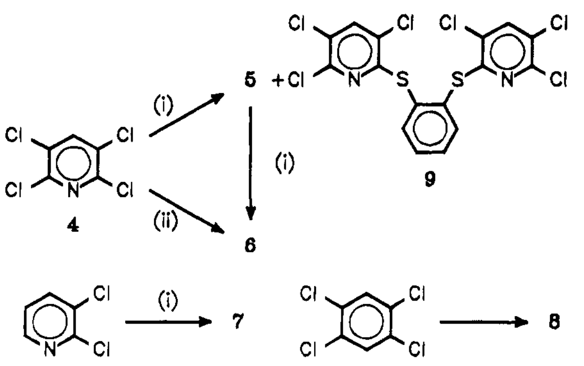
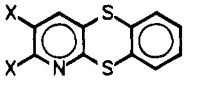
Scheme 1[a]

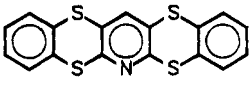


[a](i) 1 mol of 1,2-benzenedithiol, $NaHCO_3$, DMF; (ii) 2 mol of 1,2-benzenedithiol, $NaHCO_3$, DMF.

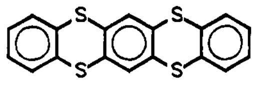
proved their synthesis using the same procedure as above and compared their physical properties with those of **5** and **6**.



**5**: X= Cl
**7**: X= H



**6**



**8**

## Results and Discussion

**Synthesis.** The preparation of the novel polycyclic heteroaromatic compound **6** was carried out by reaction of 2,3,5,6-tetrachloropyridine with 1,2-benzenedithiol (2 equiv) in dimethylformamide (DMF) and in the presence of an excess of sodium bicarbonate with a good yield. If the reaction consisted of an equimolecular mixture of 2,3,5,6-tetrachloropyridine and 1,2-benzenedithiol, 1-aza-2,3-dichlorothianthrene (**5**) was obtained as the main reaction product along with a small fraction of 2,2′-(*o*-phenylenedithio)bis(3,5,6-trichloropyridine) (**9**) as a byproduct. Thianthrene **5** is an intermediate in the synthesis of **6** because when treated with more 1,2-benzenedithiol, **5** gave **6** as the sole product (Scheme 1).

Following the same procedure, the synthesis of 1-azathianthrene (**7**) has been carried out by the reaction of 2,3-dichloropyridine with 1,2-benzenedithiol (1 equiv) with an excellent yield. It is worth mentioning that the only procedure to prepare **7** reported in the literature involved the reaction of pyridine-2,3-dithiol with 2-chloronitrobenzene in DMF and in the presence of sodium hydride, with a moderate yield.[6a]

On the other hand, the synthesis of 5,7,12,14-tetrathiapentacene (**8**) is reported as a Friedel–Crafts condensation between benzene and sulfur in the presence of $AlCl_3$, with a very low yield.[7a] We have employed a similar synthesis procedure as in case of **7** to get **8** from 1,2,4,5-tetrachlorobenzene with an improved yield.

New compounds **5** and **6** have been characterized by elemental and spectroscopic analyses. Their mass spectra showed satisfactory ion peaks which represent the base peaks due to their stability. Characterization of compounds **7** and **8** has been completed and improved.

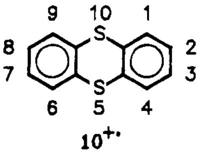
**Table 1. Experimental (Calculated) Hyperfine Coupling Constants (*G*) and other EPR Parameters for Radical Cations $7^{\bullet+}$, $6^{\bullet+}$, and $8^{\bullet+}$**

| compound | $a_H$ | $a_S$ | $g$ | $\Delta H_{pp}$ (G) |
|---|---|---|---|---|
| $7^{\bullet+}$ | 1.30 (1.28)[a] | 9.25 | 2.0081 | 0.3 |
| $6^{\bullet+}$ | 2.25 (2.24)[b]<br>0.55 (1.32)[c] | 4.7 | 2.0084 | 0.16 |
| $8^{\bullet+}$ | 0.46 (1.31)[d] | 4.8 | 2.0084 | 0.24 |

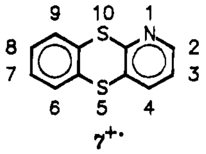
[a] Hydrogens in positions 2, 3, 7, and 8. [b] Hydrogen in position 13. [c] Hydrogens in positions 2, 3, 9, and 10. [d] Hydrogens in positions 2, 3, 6, 9, 10, and 13.

**Electron Paramagnetic Resonance (EPR).** Donor organic molecules develop their unusual properties such as electrical conductivity in the oxidized state. Thus, the oxidation of these usually aromatic systems by chemical or electrochemical procedures to their radical cations and dications has attracted increasing interest. EPR spectroscopy provides an excellent method of detecting the radical cations and it is the best way of investigating the electron distribution in their SOMO.

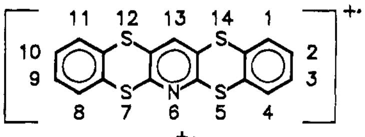
Solutions of thianthrenes in sulfuric acid[8] or in organic solvents containing Lewis acids such as $AlCl_3$ and $SbCl_5$[9] exhibit paramagnetic resonance. The formation of paramagnetic species in these systems have been interpreted as a one-electron oxidation to give radical cations.



$10^{+\bullet}$



$7^{+\bullet}$



$6^{+\bullet}$

Thus, a quintet ($a$ = 1.28 G) of quintets ($a$ = 0.135 G) has been observed in the EPR spectrum of thianthrene radical cation (**10**).[9b] Hyperfine splitting (hfs) due to coupling of the electron with naturally abundant $^{33}S$ ($I$ = 3/2, 0.76%), appears under high gain conditions ($a_S$ = 9.15 G).[9b]

The radical cations of 1-azathianthrene ($7^{\bullet+}$) and 5,7,12,14-tetrathia-6-azapentacene ($6^{\bullet+}$) generated in trifluoroacetic acid (TFAA) in the presence of Tl(III) trifluoroacetate (TTFA) are readily detected by EPR and displayed in Figures 1 and 2. TFAA has been extensively used as solvent for these oxidations[10] since its acidity and low nucleophilicity contribute to the stabilization of the radical cations formed in solution.[11]

The $g$-values are higher than that for the free electron (see Table 1), consistent with a strong spin-orbit coupling

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(8) Shine, H. J.; Piette, L. *J. Am. Chem. Soc.* **1962,** *84,* 4798. Shine, H. J.; Dair, C. F.; Small, R. J. *J. Chem. Phys.* **1963,** *38,* 569.

(9) (a) Sullivan, P. D. *J. Am. Chem. Soc.* **1968,** *90,* 3618. (b) Shine, H. J.; Sullivan, P. D. *J. Phys. Chem.* **1968,** *72,* 1390. (c) Giordan, J.; Bock, M. *Chem. Ber.* **1982,** *115,* 2548.

(10) Courtneidge, J. L.; Davies, A. G. *Acc. Chem. Res.* **1987,** *20,* 90, and references cited therein. Davies, A. G.; Juliá, L.; Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* **1989,** 239. Alemán, C.; Brillas, E.; Davies, A. G., Fajarí, Ll.; Giró, D.; Juliá, L.; Perez, J. J.; Rius, J. *J. Org. Chem.* **1993,** *58,* 3091.

(11) Depew, M. C.; Zhongli, L.; Wan, J. K. S. *J. Am. Chem. Soc.* **1983,** *105,* 2480. Davies, A. G.; McGuchan, D. C. *Organometallics* **1991,** *10,* 329.

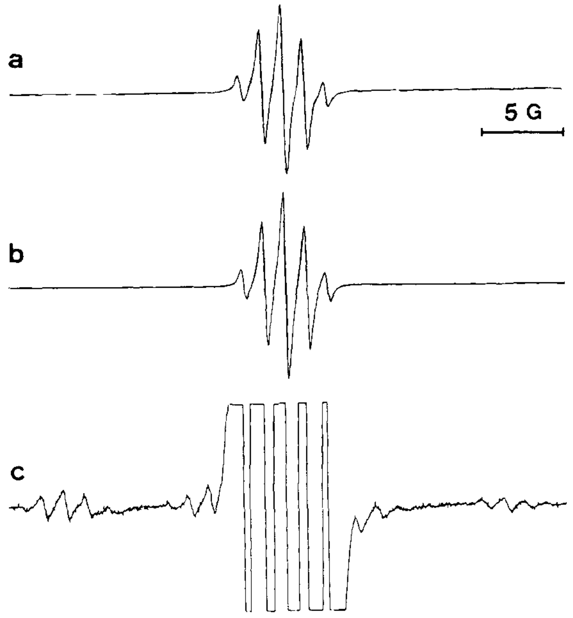


**Figure 1.** (a) EPR spectrum of 1-azathianthrene radical cation ($\mathbf{7}^{\bullet+}$) in TFAA containing TTFA. (b) Computer simulation using the data in Table 1. (c) EPR spectrum of $\mathbf{7}^{\bullet+}$ at high gain conditions; hfs constants for $^{33}$S ($I = ^3/_2$) are given in Table 1.

with sulfur atoms in the molecules, where the major spin densities reside.

1-Azathianthrene (**7**) in TFAA containing TTFA gave rise to a strong spectrum (Figure 1) consisting of a quintet (five equally spaced lines with 1:4:6:4:1 relative intensities) with the parameters listed in Table 1, and we have assigned it to the corresponding radical cation $\mathbf{7}^{\bullet+}$. hfs constants corresponding to protons in positions 2,3,7,- and 8 and that due to $^{33}$S are quite close to those from thianthrene radical cation (**10**).[9b] This observation suggests that the SOMO is only slightly modified by the introduction of the nitrogen in the molecule. Further splitting due to protons in 4, 6, and 9 has not been observed.

5,7,12,14-Tetrathia-6-azapentacene (**6**) in TFAA containing TTFA also gave a strong spectrum (Figure 2). This spectrum can be interpreted in terms of a superposition of two spectra. One of them consisted of an overlapped doublet of quintets which we have assigned to the corresponding radical cation $\mathbf{6}^{\bullet+}$ with the parameters listed in Table 1, and the other (one single line, $g = 2.00813$, $\Delta H_{pp} = 1.38$ G) corresponding to a different paramagnetic species which we have not been able to elucidate yet. In $\mathbf{6}^{\bullet+}$, the major coupling, the doublet, corresponds to the protons in position 13, and the quintets to proton in positions 2, 3, 9, and 10. Under high gain conditions, coupling with $^{33}$S appeared at approximately half the value for $\mathbf{7}^{\bullet+}$, which is accounted for by the presence of double number of sulfur atoms in the molecule.

Solutions of 5,7,12,14-tetrathiapentacene (**8**) in TFAA containing TTFA gave a weak EPR spectrum, but in $CH_2Cl_2$ containing $AlCl_3$ a much stronger one could be detected (Figure 3). Under these conditions the best simulated spectrum corresponded to the coupling of the electron with six hydrogens in the positions 2, 3, 6, 9, 10, and 13 to give a septet (seven equally spaced lines) which we have assigned to the corresponding radical cation $\mathbf{8}^{\bullet+}$. Coupling with $^{33}$S appeared at high gain conditions and its value is similar to that corresponding to $\mathbf{6}^{\bullet+}$. The EPR spectrum of the radical cation $\mathbf{8}^{\bullet+}$ in concentrated sulfuric acid was described in the literature, but a broad single line without any hyperfine splitting was then reported.[7a]

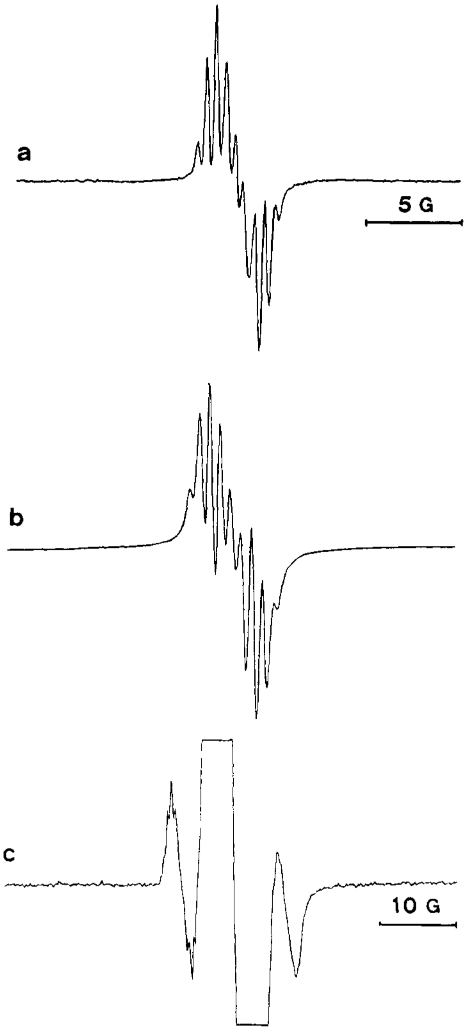
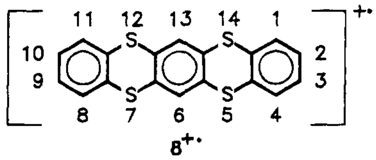


**Figure 2.** (a) EPR spectrum of 5,7,12,14-tetrathia-6-azapentacene radical cation ($\mathbf{6}^{\bullet+}$) in TFAA containing TTFA. (b) Computer simulation using the data in Table 1. (c) EPR spectrum of $\mathbf{6}^{\bullet+}$ at high gain conditions; hfs constants for $^{33}$S (I = 3/2) are given in Table 1.



$\mathbf{8}^{+\bullet}$

Theoretical estimation of the atomic spin densities for the radical cations $\mathbf{7}^{\bullet+}$, $\mathbf{6}^{\bullet+}$, and $\mathbf{8}^{\bullet+}$ has been carried out using the McLachlan method.[12] This is an extension of the Hückel LCAO-MO method in which an unrestricted wave function is used. The reliability of the results derived from McLachlan calculations depends on the selection of the appropriate heteroatom parameters. These parameters, $h_M$ and $k_{CM}$, correspond to the Coulomb integral $\alpha_M = \alpha + h_M\beta$ and the resonance integral $\beta_{CM} = k_{CM}\beta$, respectively ($\alpha$ and $\beta$ being the integrals of

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(12) McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

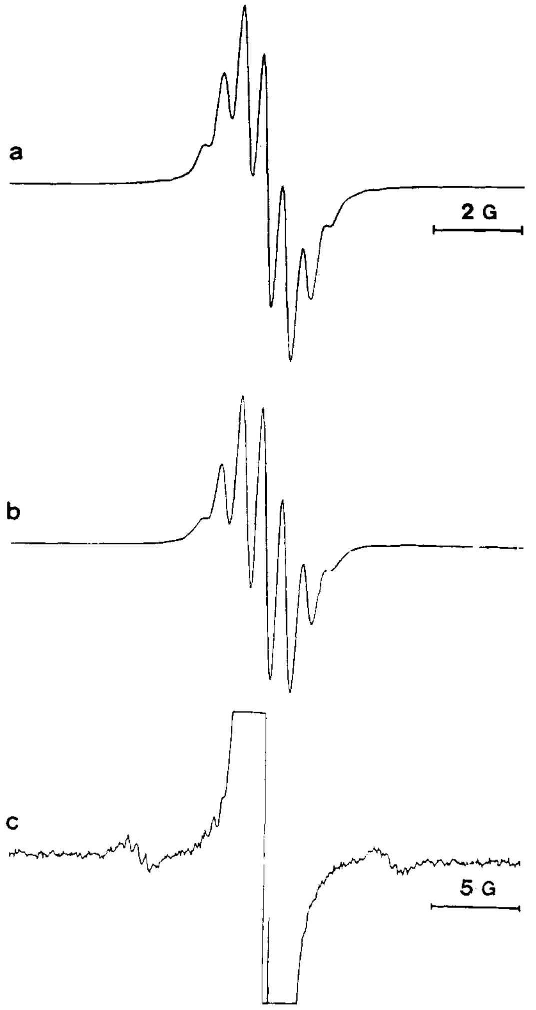


**Figure 3.** (a) EPR spectrum of 5,7,12,14-tetrathiapentacene radical cation (**8**$^{\bullet+}$) in $CH_2Cl_2$–$AlCl_3$. (b) Computer simulation using the data in Table 1. (c) EPR spectrum of **8**$^{\bullet+}$ at high gain conditions.

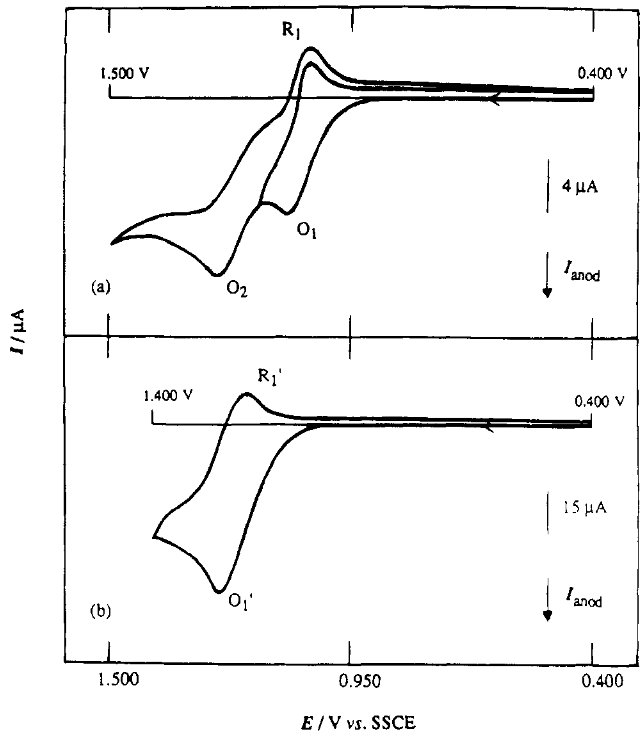
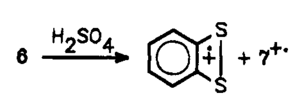


**Figure 4.** Cyclic voltammograms corresponding to the oxidation of (a) 1.0 mM **6** solution in acetonitrile with 0.1 M $LiClO_4$ on Pt, at $v$ = 50 mV s$^{-1}$, initial potential 0.400 V and reversal potentials: 1.160 V and 1.500 V; (b) 1.0 mM **7** in acetonitrile containing 0.1 M $LiClO_4$ on Pt, at $v$ = 200 mV s$^{-1}$, initial potential 0.400 V and reversal potential 1.400 V. Temperature 25.0 °C.

the carbon atom and carbon–carbon bonds, respectively, and $\alpha_M$ and $\beta_{CM}$ the integrals of the heteroatom and carbon–heteroatom bonds, respectively). The calculated spin densities were related to the experimental proton hfc constants by the McConnell equation:[13] $a_H = \varrho_C Q_{CH}H$, where $\varrho_C$ is the spin density on the nearest atom carbon and $Q_{CH}H$ is a constant set equal to 25 G.

The parameters used for sulfur atom were taken from the literature.[14] These were held fixed in all the calculations and are: $h_S = -1.20$ and $k_{CS} = 0.65$. The parameters for nitrogen atom were fitted in order to provide good hfs constants for **7**$^{\bullet+}$. The values obtained were 0.2 and 1.2 for $h_N$ and $k_{CN}$, respectively. These parameters were next applied to **6**$^{\bullet+}$, but poor agreement was found, which was attributed to the changes in the molecular environment around the nitrogen atom. Thus, the resonance integral is related with the overlap and consequently with the changes in the extension of the orbitals induced by variations in the molecular geometry.[15,16] To take into account the differences in molecular environment the value of the nitrogen–carbon resonance integral in **6**$^{\bullet+}$ should be changed. Using the $h_N$ value above, the calculations were repeated and it was found that the value of $k_{CN} = 2.0$ reproduces the proton hfs constant of **6**$^{\bullet+}$. As it can be noted, the relative magnitudes of the $k_{CN}$ parameters are physically realistic ($k_{CN}$(**7**$^{\bullet+}$) < $k_{CN}$(**6**$^{\bullet+}$)). The hfs constants computed for the different molecules are listed in Table 1. Agreement between experimental and theoretical values is reasonable.

When samples of **6** in concentrated sulfuric acid were studied by EPR, the spectra of two different magnetic species appeared at very low concentrations. One of them corresponded to the spectrum of **7**$^{\bullet+}$ and the other, consisting of a quintet ($a$ = 1.1 G; $g$ = 2.010), has been ascribed to the radical cation **11**. This chemical decomposition was found previously and reported when studying the spectra of different thianthrenes in different conditions.[9c]



**11**

**Cyclic Voltammetry (CV).** Cyclic voltammograms for the oxidation of compound **6** ($10^{-3}$ M) in acetonitrile containing $LiClO_4$ ($10^{-1}$ M) exhibited two consecutive oxidation peaks, $O_1$ and $O_2$, with similar heights. These peaks are displayed in Figure 4a, where a cyclic voltammogram at $v$ = 50 mV s$^{-1}$ in the potential interval 0.4–1.5 V is presented. On reversing the scan at potentials higher than 1.16 V (once reached the $O_1$ peak), one

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[13] McConnell, H. M.; Chesnut, D. B. *J. Chem. Phys.* **1958**, *28*, 107.
[14] Sullivan, P. D. *J. Am. Chem. Soc.* **1968**, *90*, 3618.
[15] Streitweiser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; John Wiley and Sons, Inc.: New York, 1961.
[16] Bond distances and angles in radical cations **6**$^{\bullet+}$ and **7**$^{\bullet+}$ are not known. However, they are slightly different if comparing the neutral molecules, (reference 6b and this work).

cathodic peak, $R_1$, was also found, indicating that both $O_1$ and $R_1$ peaks form a redox couple.

Peak currents of both $O_1$ and $O_2$ peaks increased linearly with the square root of the scan rate, as expected if they are diffusion-controlled.[17] However, peak current for the $R_1$ peak could not be determined accurately because $O_1$ and $O_2$ peaks overlapped partially (Figure 4a). The small difference between the first and the second oxidation potentials suggests that the intramolecular Coulomb repulsion energy is significantly low. The anodic peak potential ($E_p^a$) for the $O_1$ peak was always close to 1.10 V and the cathodic peak potential ($E_p^c$) for the $R_1$ peak was *ca.* 1.04 V. This allows one to establish that the standard potential ($E°$) of the $O_1/R_1$ couple is 1.07 V *vs* SSCE (a SCE with a NaCl-saturated aqueous solution) and that the difference between its anodic and cathodic peak potentials, ($E_p^a - E_p^c$), is about 60 mV in all $v$ tested, in agreement with the theoretical behavior expected for a reversible one-electron charge transfer reaction.[17] This couple can then be ascribed to the equilibrium reaction between **6** and its radical cation $\mathbf{6}^{\bullet+}$:

$$\mathbf{6} \rightleftharpoons \mathbf{6}^{\bullet+} + e^-$$

The fact that the $R_1$ peak is practically not observed at 20 mV $s^{-1}$ is indicative of a low decomposition rate for $\mathbf{6}^{\bullet+}$, probably by reaction with water present in the medium,[18] and hence, this species has a relative stability in solution.

On the other hand, the irreversible $O_2$ peak ($E_p^a$ = 1.25 V) must be associated with the oxidation of the radical cation $\mathbf{6}^{\bullet+}$, electrogenerated in the first oxidation process of **6** (in the $O_1$ peak), to its dication $\mathbf{6}^{2+}$. This latter species is unstable in the reaction medium and can be easily hydrolyzed by reaction with water present in solution. According to this, the following mechanism is proposed for the second oxidation process of compound **6** taking place in the $O_2$ peak:

$$\mathbf{6}^{\bullet+} \rightleftharpoons \mathbf{6}^{2+} + e^-$$

$$\mathbf{6}^{2+} \rightarrow \text{products}$$

Compound **7** ($10^{-3}$ M) in acetonitrile containing $LiClO_4$ ($10^{-1}$ M) displayed two consecutive oxidation peaks, $O'_1$ and $O'_2$, of equal height in cyclic voltammograms recorded at all $v$ tested. The peak currents of these peaks appeared near to 1.25 and 1.55 V, respectively, *i.e.* at more positive potentials than those of the respective $O_1$ and $O_2$ peaks of compound **6**. A cathodic peak, $R'_1$, associated with the $O'_1$ peak was also found at scan rates higher than 100 mV $s^{-1}$ when the potential was reversed between 1.35 and 1.50 V, prior to reaching the potential region where the $O'_2$ peak appears. On reversing the scan at potentials higher than 1.5 V, no $R'_1$ peak was observed. Figure 4b shows the cyclic voltammogram at $v$ = 200 mV $s^{-1}$ in the potential range 0.4–1.4 V where the $O'_1/R'_1$ couple can be seen. This couple had a $E°$ = 1.22 V *vs* SSCE and the difference ($E_p^a - E_p^c$) was found to be close to 60 mV, as expected for a reversible one-electron charge transfer reaction.[17] The $O'_1/R'_1$ couple can be ascribed to the reversible conversion of **7** into its radical cation $\mathbf{7}^{\bullet+}$:

$$\mathbf{7} \rightleftharpoons \mathbf{7}^{\bullet+} + e^-$$

It seems plausible to consider that radical cation $\mathbf{7}^{\bullet+}$ can be easily hydrolyzed due to the large capability of reaction between such type of species and water present in solution.[18] So, the appearance of peak $R'_1$, corresponding to the reduction of $\mathbf{7}^{\bullet+}$ to regenerate **7**, from $v$ >100 mV $s^{-1}$, can be explained assuming that this chemical reaction occurs in less extension with increasing $v$, this causing an increase in the relative amount of $\mathbf{7}^{\bullet+}$ accumulated near to the electrode.

Comparison of CV results obtained for $O_1/R_1$ and $O'_1/R'_1$ couples can be made to study the relative oxidation ability of compounds **6** and **7**. Taking into account that $E°$ ($O_1/R_1$) = 1.07 V *vs* SSCE and $E°$ ($O'_1/R'_1$) = 1.22 V *vs* SSCE, it can be concluded that compound **6** is much more easily oxidizable than compound **7**. Furthermore, CV results are indicative of a higher stability of radical cation $\mathbf{6}^{\bullet+}$ than $\mathbf{7}^{\bullet+}$, since peak $R_1$ (where reduction of $\mathbf{6}^{\bullet+}$ occurs) is found from 20 mV $s^{-1}$ whereas peak $R'_1$ (where reduction of $\mathbf{7}^{\bullet+}$ takes place) is only observed from 100 mV $s^{-1}$. This can be explained on the basis of the higher conjugation present in the molecule of **6**, which is in fact in agreement with the observation by EPR that the spin density in $\mathbf{6}^{\bullet+}$ is delocalized over the entire molecule.

Interpretation of the second oxidation process of **7** is more difficult. For $O'_2$ peak, a linear dependence of $E_p^a$ on log $v$, with a slope close to 60 mV per decade, and a difference ($E_p^a - E_{p/2}^a$) *ca.* 90 mV were found, which are in good agreement with the values predicted for an irreversible one-electron system with a transfer coefficient $\beta$ = 0.5 (theoretical values at 25.0 °C:[17] slope of the linear plot $E_p^a$ *vs* log $v$ = 59.2 mV per decade, ($E_p^a - E_{p/2}^a$) = 96 mV). The fact that the $R'_1$ peak was not observed when the scan was reversed on the potential region of the $O'_2$ peak suggests that this latter process is originated by the oxidation of a stable species formed from the chemical decomposition of the radical cation $\mathbf{7}^{\bullet+}$ electrogenerated in the $O'_1$ peak rather than the proper $\mathbf{7}^{\bullet+}$. Then, the second oxidation process of **7** is initiated by an irreversible one-electron transfer of such a stable species, which is the rate-determining step.

**Molecular and Crystal Structures of 6.** The molecular structure of compound **6** is shown in Figure 5 with the atom-numbering scheme. **6** crystallizes in the monoclinic system, space group $P2_1/c$; all bond lengths and angles (Table 2) are in the range of values found in the literature for analogous molecules.[19,23]

The asymmetric unit is half a molecule. The molecule is not centrosymmetric, but a crystallographic inversion center is found in the middle of the pyridine ring. Therefore, a positional disorder is present similarly as it has been reported for 1-azathianthrene (**7**).[6b] The aromatic rings are planar whereas the two S-containing six-membered rings adopt a boat conformation.

The S atoms deviate +0.08 Å from the pyridine mean plane, and 0.03 and 0.08 for S1 and S2′, respectively, from the benzene mean plane. The folding of the S-containing six-membered rings along S⋯S line (dihedral angle between S1, C1, C6′, S2′ and S1, C7, C8′, S2′ mean planes) is 129.9°. The pentacyclic molecule has a general chair-shaped conformation with an interplanar angle

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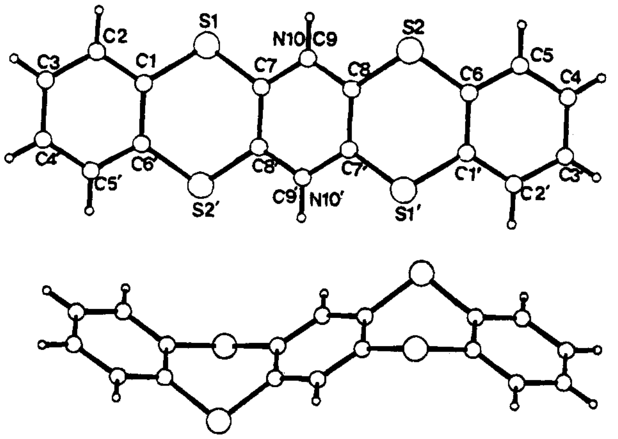

**Figure 5.** The molecular structure of 6-aza-5,7,12,14-tetrathiapentacene (**6**) with the X-ray atom-numbering scheme.

**Table 2. Selected Bond Lengths [Å] and Angles [deg] for 6**

| | |
|---|---|
| S(1)–C(7) | 1.758(2) |
| S(1)–C(1) | 1.764(2) |
| C(1)–C(2) | 1.384(3) |
| C(1)–C(6′) | 1.391(2) |
| C(2)–C(3) | 1.375(3) |
| C(3)–C(4′) | 1.376(3) |
| C(7)–N(10)/C(9) | 1.360(2) |
| C(7)–C(8′) | 1.395(2) |
| C(4)–C(3′) | 1.376(3) |
| C(4)–C(5) | 1.376(3) |
| C(5)–C(6) | 1.383(3) |
| C(6)–C(1′) | 1.391(2) |
| C(6)–S(2) | 1.764(2) |
| S(2)–C(8) | 1.761(2) |
| C(8)–N(10)/C(9) | 1.348(2) |
| C(8)–C(7′) | 1.395(2) |
| C(7)–S(1)–C(1) | 101.0(1) |
| C(2)–C(1)–C(6′) | 119.2(2) |
| C(2)–C(1)–S(1) | 118.8(2) |
| C(6′)–C(1)–S(1) | 121.9(1) |
| C(3)–C(2)–C(1) | 120.5(2) |
| C(2)–C(3)–C(4′) | 120.2(2) |
| C(9)/N(10)–C(7)–C(8′) | 120.2(2) |
| C(9)/N(10)–C(7)–S(1) | 118.0(1) |
| C(8′)–C(7)–S(1) | 121.9(1) |
| C(3′)–C(4)–C(5) | 120.1(2) |
| C(4)–C(5)–C(6) | 120.2(2) |
| C(5)–C(6)–C(1′) | 119.8(2) |
| C(5)–C(6)–S(2) | 119.1(1) |
| C(1′)–C(6)–S(2) | 121.1(1) |
| C(8)–S(2)–C(6) | 101.2(1) |
| C(9)/N(10)–C(8)–C(7′) | 120.6(2) |
| C(9)/N(10)–C(8)–S(2) | 118.2(1) |
| C(7′)–C(8)–S(2) | 121.1(1) |
| C(8)–C(9)/N(10)–C(7) | 119.3(2) |

between benzenes and the pyridine ring of 134.7(1)°, slightly greater than the analogous angle reported for 5,7,12,14-tetrathiapentacene (**8**) (131.5°).[7b] This effect is also observed when molecular structures of thianthrene and 1-azathianthrene (**7**) are compared: substitution of the carbon in the central aromatic ring for a nitrogen increases the interplanar angle (128.1° for thianthrene and 130.4° for **7**).[6b] On the other hand, this angle is higher in the pentacyclic molecules (**6** and **8**) than in the tricyclic ones (**7** and thianthrene).

The crystal packing of molecules of **6** presents a stacking pattern along the *b* axis (Figure 6a). The stacks at $z = 0$ and $z = 0.5$ are equivalent by the two-fold screw axis (Figure 6b). The shortest intrastack (d1) and interstack (d2) S⋯S contacts are 4.094 and 3.884 Å, respectively (van der Waals S⋯S distance 3.7 Å). The molecules overlap showing diagonal shifts in the stack (Figure 6c).

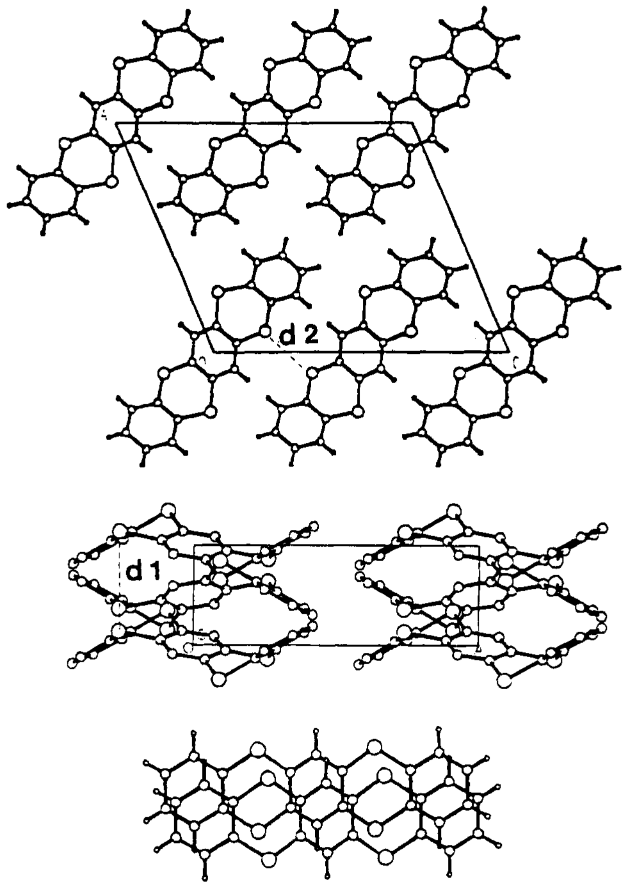

**Figure 6.** Stacking pattern in **6** as viewed along (upper) the *b* axis, (middle) the *c* axis, and (lower) molecular overlap; the view direction is perpendicular to the mean molecular plane.

**Conclusions.** We have synthesized a novel polycyclic organic compound **6**, by substitution of a nitrogen in the 6-position of 5,7,12,14-tetrathiapentacene, in a one-step reaction from 2,3,5,6-tetrachloropyridine and 1,2-benzenedithiol.

The study of the electrochemical properties of **6** by CV and the detection of its radical cation by EPR experiments, indicative of the stability of the oxidized form $\mathbf{6}^{\bullet+}$, show that **6** may be considered as a new type of electron donor to prepare radical ion salts and charge transfer complexes.

Comparative studies of the radical cations of **6** and of **8** suggest that the SOMO is greatly influenced by the introduction of the nitrogen increasing the spin-density in the central pyridine ring and, therefore, the hfc constant for the only hydrogen in this ring is much greater (2.25 G) than that of β-hydrogens in benzene rings (0.55 G). Due to the low magnetogyric ratio for the $^{14}$N nucleus, the hfc constant of the electron with the nitrogen is not enough to split further the lines of the spectrum of $\mathbf{6}^{\bullet+}$.

The X-ray structure of **6** shows that the molecule has a chair-shaped conformation and the crystal packing displays the formation of stacks with the molecules shifted in relation to the molecular mean plane normal.

Presently, we are dealing with the synthesis of the first radical cation salts of this new donor **6**. Preliminary results have shown that in anhydrous conditions a paramagnetic salt was easily obtained when mixing **6** and $SbCl_5$ in $CH_2Cl_2$. Complete characterization of this salt and preparation of others with different counterions are now in progress.

## Experimental Section

Melting points were obtained by using a Köfler microscope "Reichert" and are uncorrected. The UV spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrometer coupled with a Perkin-Elmer 7300 computer, and the IR spectra were recorded with a Perkin Elmer Model 683 spectrometer. $^1H$ NMR spectra were determined at 200 and 300 MHz with Varian Gemini 200HC and XL-300 spectrometers, respectively, and $^{13}C$ NMR spectra were recorded at 75 MHz with a Varian Gemini 300HC spectrometer. EI mass spectra were obtained on a TS-250 (VG, Manchester, U.K.) spectrometer.

**Electrochemical Measurement.** The cyclic voltammetric (CV) experiments were carried out in a three-electrode cell under an argon atmosphere. A platinum (Pt) disk with an area of 0.093 cm$^2$ was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a SSCE connected to the cell through a salt bridge containing a 0.1 M $LiClO_4$–acetonitrile solution. The temperature of test solutions and of the SSCE was kept at 25.0 ± 0.1 °C. Solutions of **6** and **7** ($10^{-3}$ M) in acetonitrile containing $LiClO_4$ (0.1 M) as background electrolyte were studied by CV. The volume of all test solutions was 25 mL. CV measurements were performed with a standard equipment consisting of a PAR 175 universal programmer, an Amel 551 potentiostat, and a Phillips 8043 X-Y recorder. Cyclic voltammograms of all solutions were recorded at scan rate ($v$) ranging between 20 and 200 mV s$^{-1}$.

**EPR Experiments.** EPR spectra were recorded with a Varian E-109 Spectrometer working in the X band. Solutions of TTFA in TFAA ($\sim 10^{-3}$ M) were added (1:1 molar proportion) to solutions of 1-azathianthrene (**7**) or 5,7,12,14-tetrathia-6-azapentacene (**6**) in TFAA ($\sim 10^{-3}$ M) and then poured into an EPR tube at room temperature. 5,7,12,14-Tetrathiapentacene (**8**) in $CH_2Cl_2$ was poured into an EPR tube at room temperature and an excess of $AlCl_3$ was added. In all cases, dissolved oxygen was removed by bubbling argon through the solutions for 5 min and then transferred to the EPR cavity. The EPR simulations were carried out with a Hewlett-Packard 9835-B computer using a modified version of the software package and a Varian E-935 Data Acquisition System.

**1-Aza-2,3-dichlorothianthrene (5).** A mixture of 1,2-benzenedithiol (2.016 g, 14 mmol), 2,3,5,6-tetrachloropyridine (3.031 g, 14 mmol), sodium bicarbonate (5 g), and DMF (150 mL) was stirred in argon at 100 °C for 2.5 h and then at reflux for 4 h. The mixture was cooled, poured into water, acidified with hydrochloric acid and then extracted with diethyl ether. The ether solution was washed with water, dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure to obtain a residue which was flash chromatographed (silica gel) eluting with *n*-hexane:chloroform (2:1) to give: (a) 1-aza-2,3-dichlorothianthrene (**5**) (2.57 g, 66%): mp 139–40 °C (recrystallized from *n*-hexane); $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 8.09 (s, 1 H), 7.59–7.53 (m, 2 H), 7.44–7.37 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 128.4, 128.5, 128.7, 129.2, 130.7, 132.0, 133.8, 137.3, 147.0, 155.5; MS *m/z* (relative intensity) 285 ($M^+$, 100), 253 (29), 250 (28), 215 (28). Anal. Calcd for $C_{11}H_5Cl_2NS_2$: C, 46.2; H, 1.8; N, 4.9; S, 22.4. Found: C, 46.0; H, 1.5; N, 4.9; S, 22.3. (b) 2,2'-(*o*-Phenylenedithio)bis(3,5,6-trichloropyridine) (**9**) (0.25 g, 5.6%): mp 179–81 °C; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.72 (dd, 2H, $J$ = 5.85, 3.6 Hz), 7.63 (s, 2H), 7.51 (dd, 2H, $J$ = 5.85, 3.6 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 126.4, 127.3, 130.5, 134.8, 137.3, 138.0, 146.3, 155.3. Anal. Calcd for $C_{16}H_6Cl_6N_2S_2$: C, 38.2; H, 1.2; N, 5.6; S, 12.8. Found: C, 38.1; H, 1.1; N, 5.6; S, 12.6.

**6-Aza-5,7,12,14-tetrathiapentacene (6).** (i) From 1-Aza-2,3-dichlorothianthrene (**5**). A mixture of 1,2-benzenedithiol (0.302 g, 2.10 mmol), **5** (0.500 g, 1.75 mmol), sodium bicarbonate (0.755 g), and DMF (23 mL) was stirred in argon at 100 °C for 1.5 h and then at reflux for 5 h. The mixture was cooled, poured into water, acidified with hydrochloric acid, and then extracted with chloroform. The organic solution, washed with water, dried over $Na_2SO_4$, and filtered, was evaporated under reduced pressure to give a residue which recrystallized from toluene and rendered 6-aza-5,7,12,14-tetrathiapentacene (**6**) (0.478 g, 77%): mp 247 °C; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.67 (s, 1H), 7.49–7.42 (m, 4 H), 7.28–7.23 (m 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 128.1, 128.2, 128.6, 129.1, 129.4, 132.7, 134.4, 134.7, 156.1; MS *m/z* (relative intensity) 355 ($M^+$, 100), 323 (34), 291 (38). Anal. Calcd for $C_{17}H_9NS_4$: C, 57.4; H, 2.6; N, 3.9; S, 36.1. Found: C, 57.4; H, 2.6; N, 4.0; S, 36.0.

(ii) From 2,3,5,6-Tetrachloropyridine. A mixture of 1,2-benzenedithiol (2.016 g, 14 mmol), 2,3,5,6-tetrachloropyridine (1.515 g, 7 mmol), sodium bicarbonate (5.0 g), and DMF (150 mL) was reacted as in i. The reaction mixture was treated as before, and the crude product was flash chromatographed (silica gel) eluting with *n*-hexane:chloroform (1:1) to give: (a) 1-aza-2,3-dichlorothianthrene (0,344 g, 16%) and (b) 6-aza-5,7,12,14-tetrathiapentacene (1.464 g, 61%). Both compounds were identified by mp and $^1H$ NMR spectra.

**1-Azathianthrene (7).** A mixture of 1,2-benzenedithiol (0.937 g, 6.5 mmol), 2,3-dichloropyridine (0.724 g, 4.96 mmol), sodium bicarbonate (2.0 g), and DMF (67 mL) was reacted as above. The reaction mixture was treated as in case of **5**, and the crude product was filtered (silica gel) eluting with chloroform to give, by recrystallization with *n*-hexane, 1-azathianthrene (**7**) (0.916 g, 85%): mp 109–10 °C (lit.[6a] 109–10 °C), identified by its $^1H$ NMR spectrum.

**5,7,12,14-Tetrathiapentacene (8).** A mixture of 1,2-benzenedithiol (0.500 g, 3.51 mmol), 1,2,4,5-tetrachlorobenzene (0.322 g, 1.49 mmol), sodium bicarbonate (1.25 g), and DMF (40 mL) was stirred in argon at 100 °C for 1 h and then at reflux for 23 h. The mixture was cooled, poured into water, acidified with hydrochloric acid, and then extracted with toluene. From the organic solution, washed with water, dried over $Na_2SO_4$, and filtered, recrystallized 5,7,12,14-tetrathiapentacene (**8**) (0.190 g, 37%): mp 325 °C; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.58 (s, 2H), 7.45 (dd, 4H, $J$ = 5.8, 3.4 Hz), 7.23 (dd, 4H, $J$ = 5.8, 3.4 Hz); exact mass calcd for $C_{18}H_{10}S_4$ ($M^+$) requires 353.9665, found 353.9675.

**Crystallographic Analysis of 6. Crystal and Intensity Data**: $C_{17}H_9N_1S_4$, MW = 355.51, monoclinic, space group $P2_1/c$ (no. 14), $a$ = 12.885(1) Å, $b$ = 4.0935(7) Å, $c$ = 15.260(2) Å, $\beta$ = 113.52(1)°, $V$ = 738.1(2) Å$^3$, $D_c$ = 1.600 g/cm$^3$, $Z$ = 2, $F$(000) = 364, $\mu$ = 6.11 cm$^{-1}$ ($\lambda$ = 0.71069 Å).

Colorless prismatic crystals were grown by vapor diffusion of ethanol into a toluene solution of **6** and from a slow evaporation of a benzene solution. The same crystal structure is observed from both methods. A suitable crystal (0.50 × 0.25 × 0.18 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo $K_\alpha$ radiation ($\lambda$ = 0.71069 Å). Lattice parameters were obtained from least-squares refinement of 25 well-centered reflections. The intensity data were collected using the $\omega/2\theta$ scan mode with $2 < 2\theta < 50°$, $hkl$ range = −15/15, 0/4, 0/18, room temperature. Standard reflections monitored every 2 h showed no significant decay. The data were corrected for Lorentz and polarization effects. No. of unique reflections = 1290.

**Structure Solution and Refinement.** The structure was solved by direct methods using the SHELXS-86 program.[20] The refinement was performed by full-matrix least-squares method on $F^2$ for all reflections using the SHELXL-93 program.[21] H-atom positions were calculated and refined with an overall isotropic temperature factor. No. of parameters = 101. $R$ = 0.0277 for 1120 $F_o > 4\sigma(F_o)$, $R$ = 0.0328 for all data (1290), $wR(F^2)$ = 0.0797 for all data. $wR(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.1403P)$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$. Largest residuals = 0.22 and −0.14

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e/Å$^3$. The geometric calculations were performed with the PARST program.[22]

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(23) The authors have deposited the atomic coordinates, thermal parameters, bond distances, and bond angles for the X-ray structure of compound **6** at the Cambridge Crystallographic Data Center. These data can be obtained on request from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge,CB2 IE2, U.K.