Novel Heterocyclic Systems. Part 27 [1].
The Synthesis of Various Diazathianthrenes and the Discrimination of Isomeric Structures using ^{13}C-NMR and Lanthanide Induced Shift Data

Charles M. Lindsay and Keith Smith*

Department of Chemistry, University College of Swansea,
Singleton Park, Swansea SA2 8PP, U.K.

Gary E. Martin

Department of Medicinal Chemistry, College of Pharmacy, University of Houston, University Park,
Houston, Texas 77004
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Syntheses of the previously unknown 1,7- 1,8- and 1,9-diazathianthrenes are reported. The former two systems were prepared *via* the condensation of the dianion of 2,3-dimercaptopyridine with 3-chloro-4-nitropyridine 1-oxide while the latter employed 2-chloro-3-nitropyridine. The preparation of the 1,9-diazathianthrene also led to the formation of the previously reported 1,6-diazathianthrene as a by-product in a 22% yield. The new ring systems were characterized by a combination of ^{13}C nmr and ^{1}H lanthanide-induced shifts using Eu(fod)$_3$.

Introduction.

Recently, the syntheses of both monoazathianthrenes have been reported [2,3]. In addition to the 2-azathianthrene parent system, a number of substituted derivatives are known, including methyl isomers, the 2-oxide, and the 4-nitro derivative, which has also been characterized by x-ray crystallography [3]. Within the 1,4-dithiinodipyridine family only two of the six possible isomers are known. Thus, the 1,6-diazathianthrene system (1,4-dithiino[2,3-*b*:5,6-*b'*]dipyridine) has been prepared and characterized by several research groups [4-7], whilst the 2,7-isomer is also described in two reports [8,9].

We now wish to report the synthesis and characterization of three of the four remaining 1,4-dithiinodipyridine systems, *viz.* 1,7-diazathianthrene (1,4-dithiino[2,3-*c*:5,6-*b'*]dipyridine), 1,8-diazathianthrene (1,4-dithiino[3,2-*c*:5,6-*b'*]dipyridine) and 1,9-diazathianthrene (1,4-dithiino-[2,3-*b*:6,5-*b'*]dipyridine). Only 2,8-diazathianthrene (1,4-dithiino[2,3-*c*:6,5-*c'*]dipyridine) now remains unknown within this family of heterocycles. Interestingly, despite the close structural similarity of the isomers that have been prepared, it proved possible unequivocally to differentiate the structures from one another by nmr spectroscopy.

Results and Discussion.

Preparation of 1,9-Diazathianthrene (3).

The preparation of 1,9-diazathianthrene (3) was accomplished by condensing the dianion of 2,3-dimercaptopyridine (1) with 2-chloro-3-nitropyridine (2). The reaction was conducted stepwise in a manner analogous to that employed in the synthesis of the corresponding 1,9-diazaphenoxathiin [5,10] and 1,9-diazaphenoxaselenin [11] (Scheme I),

using sodium hydride as the base. This gave 1,9-diazathianthrene in an isolated 59% yield accompanied by 22% of a minor product which was identified as 1,6-diazathianthrene (4) by comparison with an authentic sample. It is interesting to note that 4 is the sole product when 1 is treated with triethylamine [6]. Complete characterization of 3 by ^{1}H and ^{13}C-nmr spectroscopy is described below.

Scheme I
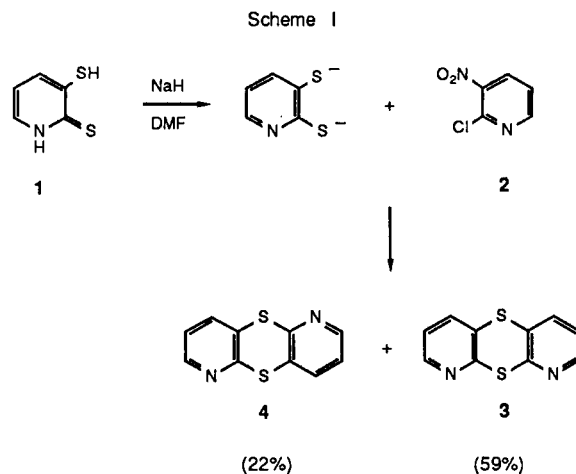
Preparation of 1,7-diazathianthrene (8) and 1,8-diazathianthrene (9).

Preparation of the 1,7- and 1,8-diazathianthrene isomers, 8 and 9, respectively was accomplished by the condensation of the dianion of 1 with 3-chloro-4-nitropyridine 1-oxide (5) prepared according to the procedure of Talik and Talik [12]. 1,7-Diazathianthrene 7-oxide (6) and 1,8-diazathianthrene 8-oxide (7) were isolated in 87% yield as an inseparable mixture following this reaction (Scheme II).

Reduction of this mixture of *N*-oxides to the parent systems was accomplished in 88% yield using phosphorus trichloride in chloroform according to the method of Ochiai [13]. The product mixture was separable by tlc, the two isomers exhibiting an Rf difference of 0.05. By careful flash column chromatography (silica, chloroform:methanol = 99.5:0.5), it was possible to obtain each isomer in pure form (ratio 45:55). Mass spectrometry showed both isomers to be diazathianthrenes, each exhibiting a characteristic molecular ion at m/z = 218 (100%, M⁺) and fragment ions corresponding to losses of HCN, CS and S. Ultimately, it was possible to differentiate **8** from **9** on the basis of a ¹H-nmr lanthanide induced shift (LIS) study which employed Eu(fod)₃. This is discussed below.

Scheme II
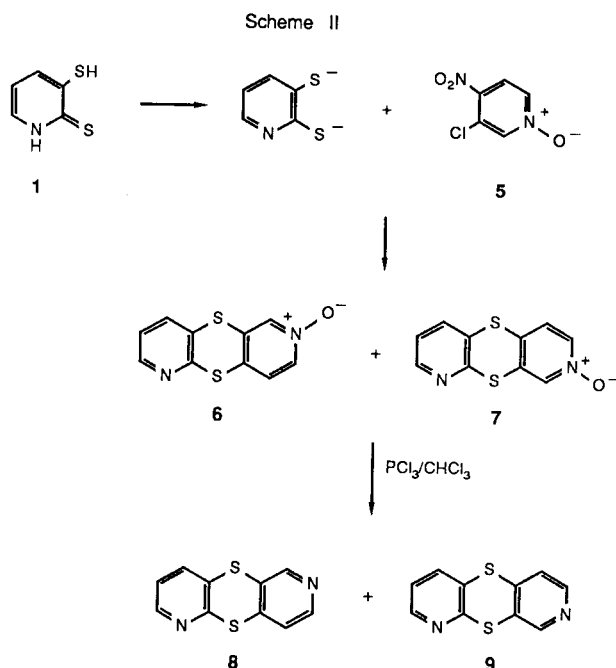
NMR Spectroscopy.

NMR Spectra of 1,9-Diazathianthrene (**3**).

The ¹H-nmr spectrum of **3** showed only three signals, at δ_H = 8.35, 7.61 and 7.09, with a clear coupling pattern corresponding to an ABX spin system. Since the compound was clearly different from the previously characterized 1,6-diazathianthrene [4-7] and exhibited this high degree of symmetry it was evident that the compound was indeed 1,9-diazathianthrene. The ¹³C-nmr spectrum showed the expected five signals, at δ_C = 156.86 (singlet in the off-resonance decoupled spectrum, C9a/C10a), 148.22 (d, C2/C8), 135.44 (d, C4/C6), 127.89 (s, C4a/C5a), and 122.27 (d, C3/C7). Although assignment of this spectrum was straightforward, it was important for the forthcoming differentiation of the 1,7- and 1,8-diazathianthrenes that an accurate method be established for calculating the chemical shift values. This was approached *via* a logical sequence of steps.

(i) The assigned ¹³C-nmr spectra of phenoxathiin [14] and 1-azaphenoxathiin [15] were used to calculate an accurate set of values for the incrementation of chemical shifts caused by aza-substituted at the 1-position of the phenoxathiin system.

(ii) These incrementations were applied to the assigned ¹³C-nmr spectrum of thianthrene [14] to provide a calculated spectrum for 1-azathianthrene which should be more accurate than has been obtained by any previous calculations [2].

(iii) The calculated chemical shifts were compared with those observed for 1-azathianthrene [2] in order to see if any of the possibly permutable assignments (C6/C9, C7/C8, and C5a/C9a) could be resolved. The results of this comparison suggested that of the three pairs of resonances originally designated as possibly permutable, two (C7/C8 and C5a/C9a) had been reported with the correct assignments but that the third pair (C6/C9) had been reversed in the assignment table [2].

(iv) The chemical shift assignments of thianthrene and the revised assignments of 1-azathianthrene were then used to derive an accurate set of chemical shift additivities for 1-aza-substitution in the thianthrene series. Since some assignments for 1-azathianthrene could still not be considered totally unequivocal, several alternative incrementation values were also calculated based on the possibly permutable assignments.

(v) The ¹³C-nmr spectrum of 1,6-diazathianthrene (**4**) was re-acquired under conditions comparable to those used in the rest of this study because of small discrepancies in the two reported spectra of this compound [5,6].

(vi) Chemical shift values were calculated for both **3** and **4** by incrementing the observed, assigned resonances of 1-azathianthrene using the 1-aza increments obtained above, arranged appropriately. Values were also calculated for the alternative assignment possibilities.

(vii) The calculated chemical shift values were compared with those actually observed for **3** and **4**. When the incrementations corresponding to the assignments indicated above were used the calculated chemical shifts for **3** and **4** fitted the observed values extremely closely (maximum discrepancy in either compound was 0.21 ppm, see Table 1). However, some of the discrepancies were much larger (typically 0.7 ppm) when any of the alternative assignments were used. Thus, this study confirms the revised assignments for the ¹³C-nmr spectrum of 1-azathianthrene and the following incrementation values ($\Delta\delta(C_i)$) for insertion of an annular nitrogen atom at the 1-position of a thianthrene: C2, 20.29; C3, −5.53; C4, 7.16; C4a, −5.03; C5a, −2.48; C6, −0.23; C7, 0.44; C8, 0.30; C9, 0.41; C9a, −0.70; C10a, 22.14 ppm. The present work further confirms the validity of additivity parameters for aza-substitution incrementations, which is important for the subsequent characterization of 1,7- and 1,8-diazathianthrenes.

Table 1

Calculated [a] *versus* Observed ^{13}C-NMR Resonance Assignments for **3** and **4** in Deuteriochloroform at 25.16 MHz

Carbon atom [b]	Calcd. **3**	Observed [c]	Observed [c]	**4** Calcd.
C2	148.12	148.22	148.05	148.26
C3	122.44	122.27	122.44	122.30
C4	135.51	135.44	136.22	136.15
C4a	127.98	127.89	129.82	129.76
C10a	156.95	156.86	155.16	155.17

[a] Calculated by inverting the resonance positions of 1-azathianthrene so that they correspond to 9- or 6-azathianthrene respectively and then incrementing for insertion of a nitrogen atom at the 1-position using the figures given in the text. [b]For each compound there are five resonances corresponding to ten carbon atoms because of symmetry. Carbon atom numbers are listed for one ring only. [c]From the spectra recorded during this study.

NMR Spectra of 1,7- and 1,8-Diazathianthrenes.

Distinction of the Isomers by ^{13}C-NMR.

The ^{13}C-nmr spectrum of 2-azathianthrene has been rigorously assigned in the pyridine ring, though not in the benzene ring [3]. By use of the data for the pyridine ring of this compound and the incrementations caused in this ring by incorporation of a 1-aza substituent in the other ring (see above) it was possible to calculate quite accurately chemical shifts for the carbon atoms in the 'right-hand' rings of compounds **8** and **9**. These could then be compared with the observed resonances (C5a through C9a) for the two isomers obtained from the preparation (isomer **A** is the chromatographically more mobile isomer). Table 2

gives the results of these calculations and provides a farly convincing indication that isomer **A** is compound **8** and isomer **B** compound **9**. It is then a simple matter to assign the remaining observed resonances for the two compounds on chemical shift grounds alone (Table 2). In order to *calculate* chemical shifts for these remaining carbon atoms it is necessary to make a decision about which of the possibly permutable assignments in 2-azathianthrene belong to which carbon atoms. The calculated values recorded in Table 2 assume the following assignments for 2-azathianthrene (*cf.* [3]): C5a, 133.21; C6, 128.95; C7, 128.03; C8, 128.25; C9, 129.14; C9a, 133.82. As can be seen from the data in Table 2, these assignments lead to very close agreement between the observed and calculated chemical shifts for the carbon atoms C2 through C4a and C10a in both compounds **A** and **B**. Permutation of any assignment in the spectrum of 2-azathianthrene would lead to interchange of the calculated shifts for the corresponding carbon atoms of **8** and **9**. Except for the case of C4 (since C1 has been replaced by nitrogen) a second interchange of the calculated values for the other resonance involved in each permutation would also have to be carried out. This leads to a significant deterioration of the fit for any of the alternative permutations. Thus, we tentatively suggest that the above assignments of the resonances of 2-azathianthrene are the most likely, and this then leads to the following calculated ^{13}C chemical shift incrementations on 2-aza substitution in the thianthrene series: C1, 19.34; C3, 20.30; C4, -5.96; C4a, 10.86; C5a, -2.28; C6, 0.37; C7, 0.50; C8, 0.72; C9, 0.56; C9a, -1.67; C10a, -3.88 ppm. These figures should be useful for calculation of chemical shifts for related compounds.

Table 2

Calculated [a] versus observed spectra for **8** and **9**

Carbon atom	Observed for **A** [b]	Calcd. for **8**	Calcd. for **9**	Observed for **B** [c]
C2	148.31	148.32 ⟶	148.54	148.51
C3	122.78	122.72 ⟵	122.50	122.76
C4	136.37	136.30 ⟶	136.11	136.10
C6	147.61	147.69 ⤬	122.39	122.56
C9	122.94	123.03 ⤬	148.33	148.24
C7	-	- ⤬	148.27	148.24
C8	147.61	148.13 ⤬	-	-
C4a	128.83	128.79 ⟶	128.18	128.30
C5a	- [d]	129.13 ⤬	143.87	143.89
C9a	146.68	145.65 ⤬	130.91	- [d]
C10a	155.32	155.35 ⟶	155.96	155.91

[a] See footnote a of Table 1 for method, but substitute incrementations for 2-aza insertion rather than for 1-aza insertion. The arrows indicate which resonances are comparable in the two calculated spectra.

[b] **A** is the faster-running isomer on tlc. The assignments listed are obtained by comparison with the calculated values on the assumption that this is the 1,7-isomer (**8**).

[c] The slower-running isomer (*cf.* footnote [b]), presumably **9**.

[d] The expected resonances were not observed.

The assignments of the structures **8** and **9** to isomers **A** and **B**, respectively, were still not considered to be unequivocal. Thus, in order to obtain further support for these structural assignments, lanthanide-shifted proton nmr spectra were also recorded.

Distinction of the Isomers by Eu-Shifted ¹H-NMR Spectroscopy.

The 100 MHz ¹H nmr spectra of isomers **A**, and **B** were almost indistinguishable, showing resonances at *ca.* δ_H = 7.2 (1H, dd, J = 5 Hz, 8 Hz, H2), 7.35 (1H, broadened doublet, J = *ca.* 5 Hz, H9 or H6), 7.7 (1H, dd, J = 8 Hz, 2 Hz, H4), 8.4 (1H, dd, J = 5 Hz, 2 Hz, H2), and 8.5 (2H, very broad, H6 and H8 or H7 and H9). A series of spectra was then measured (deuteriochloroform) with serial additions of Eu(fod)₃, after which the observed chemical shift of each resonance was plotted against the amount of shift reagent added. Figures 1 and 2 show the least squares fitted curves obtained [16]. (The line representing the greatest shifts of isomer **A** corresponds to two protons.)
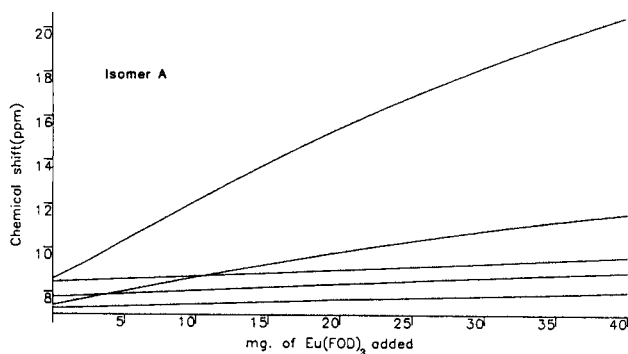

Figure 1. Effect of added shift reagent on the proton nmr chemical shifts of isomer **A**.
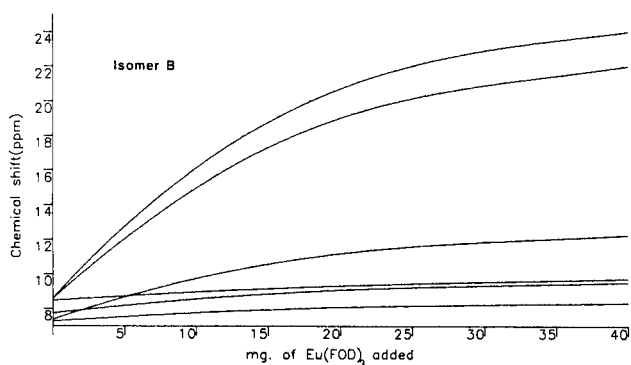

Figure 2. Effect of added shift reagent on the proton nmr chemical shifts of isomer **B**.

As is evident from Figures 1 and 2, complexation occurs predominantly at N7 or N8 rather than at N1. Furthermore, at higher concentrations of shift reagent, the initially almost linear relationships develop increased curvature which probably reflects an approach to saturation at

N7 or N8 accompanied by increasing complexation at N1. Thus, relative europium-induced shifts for the different protons in each molecule were determined from the slopes of the lines over the early linear part of the range. All values were normalized to be relative to the shift induced in H3, which moved least in both isomers. The results are shown in Table 3.

Table 3

Calculated and Observed Eu-Induced Relative Shifts [a]

Proton	Observed shifts		Calculated shifts	
	Isomer **A**	Isomer **B**	**8**	**9**
H2	1.32	1.03	1.47	1.17
H3	1.00	1.00	1.00	1.00
H4	1.49	1.70	1.44	1.55
H6/H9 [b]	17.8	15.6	17.1	14.2
H8/H7 [b]	17.8	13.3	16.1	14.2
H9/H6 [b]	6.35	4.92	6.40	5.72

[a] Calculated as described in the text, all values normalized on H3.
[b] The first member of the pair if the structure is **8** and the second if the structure is **9**.

It was then necessary to calculate relative shifts expected for the two isomers. In order to be able to do so a full geometrical structure of each molecule was generated by using typical bond lengths and angles from thianthrene [17] and monoazathianthrene [3,17] crystal structures. The actual bond distances and angles used are shown in Figure 3. In order to accomodate these geometrical parameters, the central dithiin ring in each case must adopt a dihedral angle (folding angle) of 132°. Europium was placed at position 7 or 8 as indicated in Figure 3, the principle magnetic axis was assumed to lie along the N-Eu bond. All Eu-H distances (r) and N-Eu-H angles (θ) were calculated and a series of relative shifts for the various hydrogen atoms in each molecule was calculated using the McConnell-Robertson equation [18]:
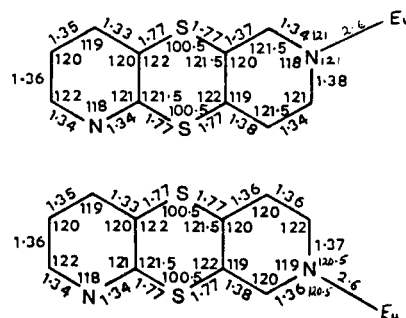
$$\Delta\delta = Kr^{-3}(3\cos^2\theta - 1).$$

Figure 3. Bond lengths and angles used to generate calculated structures for 1,7- and 1,8-diazanthianthrenes for purposes of calculation of Eu(fod)₃-shifted spectra.

This treatment produced a series of relative proton shifts which fitted better for the assignment of isomers already indicated by the ^{13}C-nmr study than for the alternative assignment, but the errors when compared with the observed were still relatively large even for the favored assignments. Thus, the values were recalculated on the assumption that a small amount of coordination of the europium atom to position N1 of each molecule was occurring. Optimal fit of the data was obtained for approximately 2.5% of the coordination occurring at N1. The results of this calculation are presented alongside the observed values in Table 3.

As can be seen from the table, the fit is much more acceptable if isomer **A** is the 1,7-isomer **8** and isomer **B** the 1,8-isomer **9** than for the alternative assignments. Thus, the magnitude of the shift of H4 relative to H3 is calculated to be greater for **9** than for **8** and the observed relative shift for isomer **B** is greater than that for **A**. Also, the calculated shifts, relative to H3, for H2, H6, H8 and H9 in **8** are all calculated to be greater than the comparable values for H2, H6, H7 and H8 in **9**. In each case the observed shifts are indeed greater for isomer **A** than for **B**. The absolute values of the calculated shifts could almost certainly have been brought even closer to the observed values by small modifications of the assumed geometries of the molecules, but since the results already provided adequate support for the assignments indicated by ^{13}C-nmr further refinement was deemed unnecessary.

Conclusion.

All four 1,n-diazathianthrenes with n = 6, 7, 8 or 9 have now been obtained. The structures of the isomers have been confirmed by ^{13}C-nmr and, in the case of the 1,7- and 1,8-isomers, europium-shifted proton nmr studies. Two series of ^{13}C-nmr incrementation parameters, for 1-aza and 2-aza annular substitution in a thianthrene, have been derived, and these should prove extremely useful for accurate calculations of chemical shift values for related azathianthrenes.

EXPERIMENTAL

Melting points were obtained using a Gallenkamp hot-stage apparatus and are reported uncorrected. The ir spectra were obtained as potassium bromide discs on a Pye-Unicam SP1050 spectrophotometer. [1]H- and ^{13}C-nmr spectra were recorded in deuteriochloroform on Varian HA-100 (proton) or Varian XL-100 (carbon) spectrometers operating at observation frequencies of 100.06 and 25.16 MHz, respectively. Chemical shifts for diazathianthrenes are recorded in Tables 1 and 2 and in the text. Mass spectra were recorded under electron impact using a modified Kratos MS9 instrument.

Preparaton of 1,9-Diazathianthrene (**3**) and 1,6-Diazathianthrene (**4**).

A 100 ml, two-necked, round-bottomed flask was charged rapidly with oil-free sodium hydride (0.5 g, excess, obtained by washing an 80% dispersion in oil with pentane). It was then fitted with a septum on the side arm and a septum-capped reflux condenser, cooled in ice and flushed with dry nitrogen. Dry N,N-dimethylformamide (DMF, 5 ml) was add-

ed and the suspension was stirred during addition of **1** (1.00 g, 7.0 mmoles) in 10 ml of DMF. To the stirred mixture was added, slowly over 20 minutes, a solution of **2** (1.11 g, 7.0 mmoles) in 15 ml DMF. The stirred mixture was allowed to warm to ambient temperature overnight and was then brought to reflux for 5 hours. The reaction mixture was allowed to cool then poured into distilled water (150 ml) and extraced with chloroform (8 × 15 ml). The combined extracts were washed with aqueous sodium carbonate (2 × 20 ml of 0.5M) and distilled water (2 × 20 ml) and then dried over magnesium sulfate. Concentration under reduced pressure gave an oily solid which was purified by flash-column chromatography on silica (methanol:chloroform, 5:95). This produced **3** (0.90 g, 51% after recrystallization), and **4** (0.34 g, 22% after recrystallization from chlroform). The latter compound was identical to samples of **4** prepared previously, mp 183-185° (lit 183-185° [4], 186-188° [5]). The former was recrystallized from chloroform to give **3** as off-white crystals, mp 184-186°; ms: m/z (% relative intensity) = 219 (14), 218 (100, M⁺), 186 (21), 174 (38), 109 (11), 82 (17), 69 (14), 39 (26).

Anal. Calcd. for $C_{10}H_6N_2S_2$: C, 55.04; H, 2.75: N, 12.84. Found: C, 55.14; H, 2.61; N, 12.71.

Preparation of a Mixture of 1,7-Diazathianthrene 7-Oxide (**6**) and 1,8-Diazathianthrene 8-Oxide (**7**).

The dianion of **1** (7.0 mmoles) was generated as above from **1** and sodium hydride in DMF (30 ml). A solution of 3-chloro-4-nitropyridine 1-oxide (**5**, 1.22 g, 7.0 mmoles), prepared according to the procedure of Talik and Talik [12], in DMF (25 ml) was added and the mixture was stirred at ambient temperature overnight, then brought to reflux for 7.5 hours. The mixture was cooled and distilled water (150 ml) was added slowly. The resulting solution was extracted with dichloromethane (6 × 50 ml) and the combined extracts were washed with 10% sodium carbonate solution (2 × 30 ml) followed by water (5 × 15 ml) and then dried over magnesium sulfate. Concentration under reduced pressure gave a crude product (87%) which was purified by flash-column chromatography over silica (methanol:chloroform, 7.5:92.5). Chromatography yielded a mixture of **6** and **7** (1.20 g, 73%) which was free of other components. The mixture was recrystallized from cyclohexane-ethyl acetate without separation of the mixture, mp - partial melting at 219° and melting properly at 240-241°; [1]H-nmr: δ_H = 8.5 (m), 7.9-8.2 (m), 7.5 (m), ^{13}C-nmr: δ_c = 154.7, 153.9, 148.0, 138.1, 137.3, 136.8, 133.7, 132.0, 131.2, 129.6, 128.3, 127.1, 124.8, 124.6, 123.4 (some superimposed resonances); ms: m/z (% relative intensity) 234 (100, M⁺), 218 (37), 217 (20), 204 (25), 191 (41), 178 (19), 82 (32), 69 (55).

Anal. Calcd. for $C_{10}H_6N_2OS_2$: C, 51.28; H, 2.56; N, 11.96. Found: C, 51.55; H, 2.45; N, 11.76.

Preparation of 1,7-Diazathianthrene (**8**) and 1,8-Diazathianthrene (**9**).

A mixture of **6** and **7** obtained as above (0.304 g, 1.3 mmoles) was dissolved in chloroform (20 ml). Phosphorus trichloride (0.55 g, excess) was added slowly and the mixture was then refluxed for 7 hours [13]. The mixture was cooled and carefully added to water (50 ml). The solution was neutralized to pH 7 with 5M sodium hydroxide and then extracted with chloroform (3 × 15 ml). The combined chloroform extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give an off-white solid (0.25 g, 88% yield). Flash column chromatography on silica (methanol:chloroform = 0.5:99.5) allowed separation of the isomers to give **8** (0.11 g) and **9** (0.13 g). The nmr characterization of these components is discussed in detail in the text. Other analytical data are given below.

Compound **8**.

This compound had mp 120-121°; ms: m/z (% relative intensity) = 218 (100, M⁺), 191 (29), 174 (16), 96 (21), 82 (15), 39 (13).

Anal. Calcd. for $C_{10}H_6N_2S_2$: C, 55.04; H, 2.75; N, 12.84. Found: C, 55.35; H, 2.50; N, 12.79.

Compound **9**.

This compound had mp 119-120°; ms: m/z (% relative intensity) = 218 (100, M⁺), 191 (36), 185 (17), 174 (24), 96 (13), 82 (28), 69 (19), 39 (20).

Anal. Calcd. for $C_{10}H_6N_2S_2$: C, 55.04; H, 2.75; N, 12.84. Found: C, 55.35; H, 2.62; N, 12.76.

REFERENCES AND NOTES

[1] For Part **26** in this series, see C. M. Lindsay, K. Smith, and G. E. Martin, *J. Heterocyclic Chem.*, **24**, 211 (1987). The current paper also represents Part **XXXV** in the series "Chemistry of the Phenoxathiins and Isosterically Related Heterocycles".

[2] S. Puig-Torres. G. E. Martin, J. J. Ford. M. R. Willcott and K. Smith *J. Heterocyclic Chem.*, **19**, 1441 (1982).

[3] W. W. Lam, G. E. Martin, V. M. Lynch, S. H. Simonsen, C. M. Lindsay and K. Smith, *J. Heterocyclic Chem.*, **23**, 785 (1986).

[4] M. Edrissi, H. Kooshkabadi and I. Lalezari, *Microchem. J.*, **19**, 282 (1974).

[5] J. S. Davis, K. Smith, J. R. Turner and G. Gymer, *Tetrahedron Letters*, 5035 (1979).

[6] S. Puig-Torres, C. H. Womack, G. E. Martin, M. R. Willcott and K. Smith, *J. Heterocyclic Chem.*, **19**, 1561 (1982).

[7] S. Puig-Torres, G. T. Gampe, Jr., G. E. Martin, M. R. Willcott and K. Smith, *J. Heterocyclic Chem.*, **20**, 253 (1983).

[8] K. Krowicki and P. Nantka-Namirski, *Rocz. Chem.*, **51**, 2485 (1977).

[9] K. Krowicki, *Pol. J. Chem.*, **52**, 2039 (1978).

[10] S. R. Caldwell, J. C. Turley and G. E. Martin, *J. Heterocyclic Chem.*, **17**, 1153 (1980).

[11] K. Smith, I. Matthews and G. E. Martin, *J. Chem. Soc., Perkin Trans. I*, in press.

[12] T. Talik and Z. Talik, *Rocz. Chem.*, **36**, 539 (1962).

[13] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

[14] S. Puig-Torres, M. S. Thesis, Houston, 1982.

[15] G. E. Martin, J. C. Turley and L. Williams, *J. Heterocyclic Chem.*, **14**, 1249 (1977).

[16] Program supplied by A. Mehta, Department of Chemical Engineering, University College of Swansea.

[17] S. B. Larson, S.H. Simonsen, G. E. Martin, K. Smith and S. Puig-Torres, *Acta Cryst.*, **C40**, 103 (1984).

[18] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); we have previously used this approach to distinguish the structures of some isomeric betaines [19].

[19] K. Smith, J. R. Turner, J. S. Davies, S. R. Byrn and A. T. McKenzie, *J. Chem. Res.*, (S) 107; (M) 1320 (1981).