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The synthesis of 2-azathianthrene ([1,4]benzodithiino[2,3-*c*]pyridine), the only remaining monoazathianthrene yet to be reported, is described. Attempts at the direct condensation of disubstituted pyridines with the dianion of 1,2-dimercaptobenzene were generally unsuccessful requiring that the alternative condensation of the dianion with disubstituted pyridine 1-oxides be employed. The title compound was characterized by physical means including ¹³C-nmr spectroscopy. One analog, 4-nitro-2-azathianthrene was also studied by X-ray crystallographic means; the molecule crystallized with two molecules in the asymmetric unit P2₁/*n*, *a* = 20.712(3), *b* = 7.8109(13), *c* = 13.720(2) Å, β = 107.880(11)°, *Z* = 8, the data refined to a final *R* = 0.051 for 3061 reflections. Dihedral angles between the planes of the phenyl rings were 135.00(13) and 132.52(13)° for the two independent molecules contained in the crystal. Close non-bonded S...O intramolecular contacts were observed in both molecules between the sulfur and nitro-group oxygens. Both nitro groups are twisted out of the plane of the pyridine ring and are oriented at angles of 28.75 and 38.82° respectively.

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Introduction.

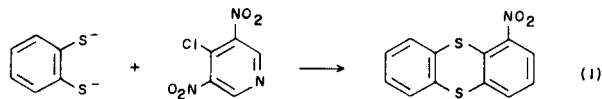
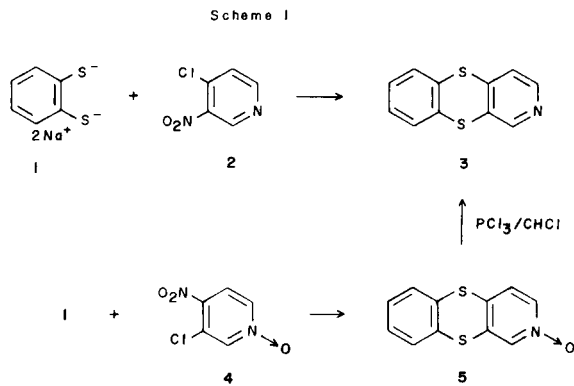
Despite the reported syntheses of numerous azaphenothiazine and azaphenoxazine analogs [2] and the synthesis of all four possible monoazaphenoxathiin analogs [3-6], the first report of a monoazathianthrene appeared only in 1982 [7]. Thus, 1-azathianthrene was prepared by the condensation of the dianion of 3-mercaptopyridine-2(1*H*)-thione with 2-nitrochlorobenzene in a 45% yield. The remaining monoazathianthrene, 2-azathianthrene remains unknown.

Synthetically, 2-azathianthrene (**3**) should be accessible by either of two alternative routes as shown in Scheme I. Direct condensation of the dianion **1** with 4-chloro-3-nitropyridine (**2**) has been employed with good success in the

synthesis of the isosterically equivalent 3-azaphenoxathiin system [5]. Similarly, the condensation of **1** with 3-chloro-4-nitropyridine-1-oxide (**4**) has also been successfully employed in the synthesis of the 2-azaphenoxathiin system [4]. Hence, either of these alternative routes should permit the successful preparation of the desired 2-azathianthrene (**3**), the latter affording the desired parent system in one additional step after reduction of the 2-oxide of **5** using phosphorus trichloride in chloroform according to the method of Ochiai [8].

Results and Discussion.

Initially, there was no reason to favor either of the two possible routes leading to the desired 2-azathianthrene (**3**) system. Thus, we elected to pursue the synthesis directly *via* the condensation of the dianion of 1,2-dimercaptobenzene prepared *in situ* with sodium hydride with 4-chloro-3-nitropyridine (**2**) prepared according to the procedure of Kruger and Mann [9]. Repeated attempts using this procedure failed to give the desired system in anything other than trace amounts with a propensity toward the formation of the dibenzotetrasulfide by oxidative dimerization of the dianion. In contrast, condensation of **1** with 4-chloro-3,5-dinitropyridine gave the corresponding 4-nitro-2-azathianthrene (**7**) in a yield of 92% shown in Equation 1.



(1)

Following the failure of the direct condensation route to 2-azathianthrene (**3**), the alternative route *via* the 2-azathianthrene 2-oxide (**5**) was instead employed. Using this approach, the dianion, **1**, was condensed with 3-chloro-4-nitropyridine 1-oxide (**4**) prepared according to the method of Talik and Talik [10] to afford the required 2-azathianthrene 2-oxide (**5**) in 64% yield. Although **5** was the main product of the reaction, a small quantity (3%) of a compound with a mass-spectrum corresponding to a diazathianthrene was also isolated as a byproduct of the reaction. Reduction of the 2-oxide using phosphorus trichloride in chloroform [8] gave the desired 2-azathianthrene parent ring system in a 76% yield (49% overall). In similar fashion, reaction of the dianion of toluene-3,4-dithiol gave an inseparable mixture of the 7- and 8- methyl isomers of the 2-azathianthrene 2-oxide and 2-azathianthrene systems in an overall yield of 84%.

Preliminary characterization of the 4-nitro-2-azathianthrene (**7**) prepared according to Equation 1 was obtained by mass spectral analysis. Thus, **7** gave a molecular ion, M^+ , at $m/z = 262$ (45%) with characteristic fragment ions corresponding to a loss of the nitro group, loss of HCN and loss of sulfur. Similarly, the 2-azathianthrene 2-oxide (**5**) gave a molecular ion, M^+ , at $m/z = 233$ (100%) with a characteristic loss of the 2-oxide functionality. Finally, the parent 2-azathianthrene (**3**) obtained by the reduction of **5** also gave a molecular ion, M^+ , at $m/z = 217$ (100%) with characteristic fragment ions from the loss of HCN and sulfur.

NMR Spectroscopy.

Confirmation of the location of the annular nitrogen atom at the 2-position was afforded by both ^1H - and ^{13}C -nmr spectroscopic data. Thus, the 100 MHz ^1H -nmr spectrum of **3** contained a singlet resonating at 8.53 ppm and a doublet at 8.24 ppm which were attributable to the H1 and H3 resonances respectively. The balance of the protons constituted a complex multiplet centered at 7.35 ppm which was not interpreted.

Total and unequivocal assignment of the ^{13}C -nmr spectrum of **3** was not possible. The difficulty inherent in the assignment of the carbon nmr spectrum is largely due to the highly similar nature of the chemical environments of many of the carbons in the structure. Thus, the four quaternary carbons resonated at 146.35, 133.82, 133.21 and 131.61 ppm and only the β carbon resonating at 146.35 ppm could be assigned with certainty. The α carbon can be assigned tentatively as the quaternary carbon resonating at 131.61 ppm on the basis of chemical shift additivity considerations associated with the insertion of the annular nitrogen atom. The remaining two quaternary carbon resonances could not be assigned with any degree of assurance.

Within the protonated carbon group, the carbons of the

pyridine derived portion of the molecule were assignable on the basis of chemical shift and spin-lattice (T_1) relaxation considerations. Thus, on the basis of chemical shift, the C1, C3 and C4 resonances were identifiable as the protonated carbons resonating at 147.92, 147.83 and 122.62 ppm. The balance of the protonated carbons are reflective of the largely symmetrical nature of the molecule, with all four carbons resonating within essentially a 1.1 ppm wide region (129.14, 128.95, 128.25 and 128.03 ppm). Clearly, the C4 resonance may be assigned at 122.62 ppm on the basis of the effects of annular nitrogen insertion into the ring. Discriminating between the C1 and C3 resonance assignments when these resonances differ in chemical shift by only 0.09 ppm is clearly not possible unless other data is considered. Similarly, beginning to make any assignments within the protonated carbon group for the benzene ring cannot be attempted unless additional information is available.

To make an inroad into the problem of assigning the remaining protonated carbon resonances of **3**, two alternative approaches are available: utilization of two-dimensional nmr methods or T_1 relaxation data. The former, employing the combined utilization of proton-carbon heteronuclear chemical shift correlation [11,12] and relayed coherence transfer [13-16] has been successfully used to assign a number of polynuclear aromatic systems [17-20]. Unfortunately, in the case at hand, the congestion of both the proton and carbon spectra is so high that the heteronuclear relay experiment would not allow the observation of the responses arising from the vicinal transfer of magnetization which would be necessary to employ the technique successfully. The utilization of carbon-carbon double quantum coherence techniques [18,21] would similarly be difficult to employ because of the nearly exclusive AB character expected for the protonated carbons of the benzene ring. Thus, it appeared that the utilization of T_1 relaxation data offered the best chance of obtaining at least a partial assignment of the ^{13}C -nmr spectrum of **3**.

Anisotropic reorientation of heterotricyclic systems has been shown to have a predictable effect on carbon T_1 relaxation times irrespective of the molecular dihedral angle of the system under study [7,22-24]. Spin-lattice relaxation time measurements obtained using the inversion recovery pulse sequence [25,26] with data reduction using the three parameter fitting program of Kowalewski and co-workers [27] gave two readily discernible groups. The more rapidly relaxing group of carbons exhibited a T_1 relaxation time of 3.13 \pm 0.12 seconds while the less efficient group averaged 3.96 \pm 0.25 seconds. Based upon this observed behavior, the protonated carbon resonating at 147.92 ppm with a measured T_1 of 4.28 seconds was assigned as C1 with a C-H bond vector oriented at -90° to the axis of anisotropic reorientation while the carbon resonating at

147.83 ppm with a measured T_1 of 3.26 seconds was assigned as C3. Despite the utility of the spin-lattice relaxation data in assigning the pyridine derived carbons, the protonated carbons of the benzene ring can be subgroup assigned but cannot be assigned any further. Thus, the resonances at 128.25 and 128.03 ppm with relaxation times of 3.03 and 3.09 seconds respectively were attributable to the C7 and C8 resonances; the resonances at 129.14 and 128.95 ppm with relaxation times of 4.01 and 3.71 seconds were ascribed as the C6 and C9 carbon resonances. Within the individual pairs, however, unequivocal assignments cannot be made. Finally, from the observed relaxation data, the 2-azathianthrene nucleus was found to have a tumbling preference ratio, $P = 1.92$, which compares favorably with that of the related 1-azathianthrene system [7].

Molecular Structure.

One of our interests in the thianthrene system is directed toward studying the effects that substituents in or on the aromatic rings have on the geometry of the molecule. We are particularly interested in the influence of substituents on the molecular dihedral angle and the changes in other parameters, *e.g.* the C-C-S and C-S-C angle to accommodate changes in the dihedral angle. Unfortunately, repeated attempts to obtain suitable crystals of the parent 2-azathianthrene (**3**) ring system were uniformly unsuccessful. However, we did obtain satisfactory crystals of the 4-nitro analog **7**. Interestingly, **7** affords us with the opportunity of examining both the effects of annular aza-substitution at the 2-position and the effects of sulfur-nitro group non-bonded interactions. Rosenfield, Parthasarathy and Dunitz [28] have reported that there seems to be a directional preference for atoms making close non-bonded contacts with divalent sulfur. Furthermore, there appears

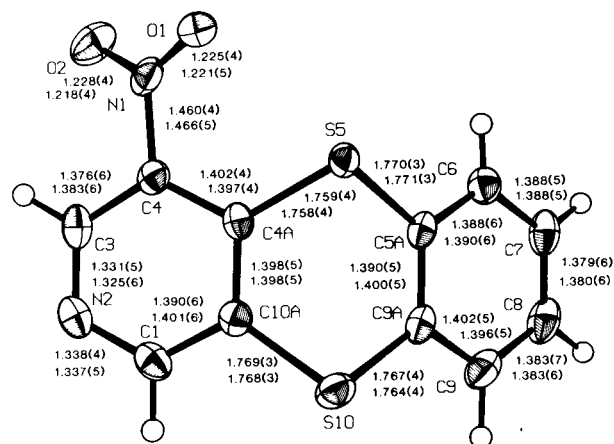


Figure 1. View of molecule I in the crystal of 4-nitro-2-azathianthrene showing atom labelling scheme with bond distances between the non-H atoms. Values for atoms of molecule II are given below those of molecule I for ease of comparison.

Table 1
Positional and Thermal Parameters for 4-Nitro-2-azathianthrene

Atom	X	Y	Z	Ueq, Uiso [a]
S(5)	.2311(4)	.07975(12)	.14674(6)	.0231(3)
S(10)	.27539(5)	.08736(13)	.39612(7)	.0296(3)
S(5')	.23810(4)	.15529(12)	.64834(7)	.0256(3)
S(10')	.28094(4)	.14758(13)	.89689(7)	.0281(3)
C(1)	.1538(2)	-.0667(5)	.3710(3)	.0290(13)
N(2)	.09157(15)	-.1269(4)	.3235(2)	.0317(12)
C(3)	.0719(2)	-.1252(5)	.2216(3)	.0298(14)
C(4)	.1120(2)	-.0622(5)	.1662(3)	.0225(11)
C(4a)	.1771(2)	.0028(4)	.2139(3)	.0208(11)
C(5a)	.3108(2)	.0041(4)	.2247(3)	.0229(12)
C(6)	.3551(2)	-.0573(5)	.1746(3)	.0277(13)
C(7)	.4204(2)	-.1048(5)	.2314(3)	.0341(15)
C(8)	.4407(2)	-.0982(5)	.3369(3)	.0363(15)
C(9)	.3962(2)	-.0448(5)	.3879(3)	.0336(14)
C(9a)	.3310(2)	.0096(4)	.3310(3)	.0248(12)
C(10a)	.1974(2)	-.0009(4)	.3209(3)	.0228(12)
N(1)	.08428(14)	-.0607(4)	.0547(2)	.0282(11)
O(1)	.10381(12)	.0510(4)	.0076(2)	.0357(10)
O(2)	.04197(13)	-.1700(4)	.0140(2)	.0457(11)
C(1')	.1561(2)	.2916(5)	.8700(3)	.0306(14)
N(2')	.09364(15)	.3478(4)	.8205(3)	.0350(13)
C(3')	.0760(2)	.3493(5)	.7191(3)	.0342(15)
C(4')	.1181(2)	.2923(5)	.6649(3)	.0258(12)
C(4a)'	.1829(2)	.2286(4)	.7144(3)	.0219(12)
C(5a)'	.3161(2)	.2403(4)	.7265(3)	.0241(12)
C(6)'	.3598(2)	.3084(5)	.6774(3)	.0276(13)
C(7)'	.4230(2)	.3699(5)	.7346(3)	.035(2)
C(8)'	.4422(2)	.3643(5)	.8402(3)	.0343(14)
C(9)'	.3986(2)	.3011(5)	.8902(3)	.0311(14)
C(9a)'	.3354(2)	.2363(4)	.8336(3)	.0239(12)
C(10a)'	.2018(2)	.2295(4)	.8214(3)	.0239(12)
N(1')	.09295(14)	.2975(4)	.5527(2)	.0300(11)
O(1')	.10813(13)	.1787(4)	.5062(2)	.0407(11)
O(2)'	.0597(2)	.4215(4)	.5127(2)	.0573(13)
H(C1)	.169(2)	-.070(5)	.448(3)	.047(13)
H(C3)	.028(2)	-.166(5)	.186(3)	.030(10)
H(C6)	.338(2)	-.060(5)	.103(3)	.040(12)
H(C7)	.449(2)	-.145(5)	.196(3)	.041(12)
H(C8)	.486(2)	-.129(5)	.378(3)	.055(13)
H(C9)	.410(2)	-.039(5)	.466(3)	.033(11)
H(C1')	.171(2)	.287(5)	.948(3)	0.42(12)
H(C3')	.033(2)	.385(5)	.680(3)	.050(13)
H(C6)'	.3471(14)	.320(4)	.607(2)	.011(8)
H(C7)'	.454(2)	.410(5)	.701(3)	.041(12)
H(C8)'	.483(2)	.403(5)	.883(3)	.032(11)
H(C9)'	.4111(15)	.300(4)	.962(2)	.014(9)

[a] For anisotropic atoms, the U value is U_{eq} , calculated as

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i \cdot a_j$$

where A_{ij} is the dot product of the i^{th} and j^{th} direct space unit cell vectors.

to be a difference in whether the atom making contact is a potential Lewis acid (metal ions, for example) or Lewis base (halide ions or the oxygen of a nitro group, for example). Close contacts by Lewis bases generally tend to be along the extension of one of the bonds to sulfur (*e.g.* S-X). It was suggested that this orientation was stabilized by an interaction between the Lewis base and a $\sigma^*(S-X)$ orbital on sulfur. The 4-nitro-2-azathianthrene (**7**) clearly falls into

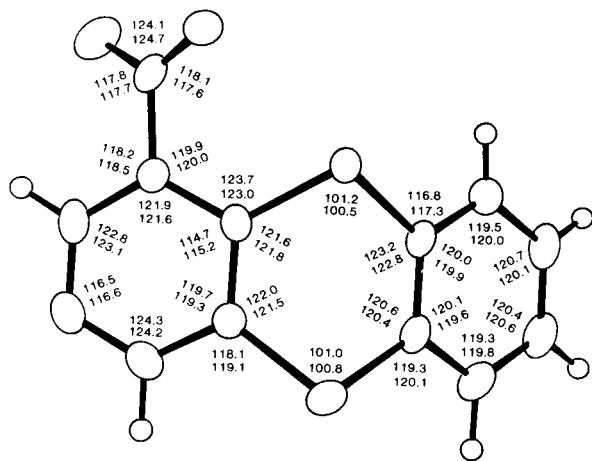


Figure 2. View of molecule I of 4-nitro-2-azathianthrene, showing bond lengths and angles ($^{\circ}$). Values for molecule II are given below those of molecule I for ease of comparison.

this group and provides a chance to examine the potential effects of this type of interaction in the thianthrene series further.

The compound crystallized with two different molecules (I and II) in the unit cell. Positional and thermal parameters are listed in Table 1. Atoms labelled with a' are those from molecule II. The atom labelling scheme with bond distances is shown in Figure 1, while the bond angles are shown in Figure 2. A view of the molecular packing is shown in Figure 3. Columns of I and II are arranged in a checker board pattern with their mean molecular planes being nearly parallel to *ac*, with I inclined by $4.12(3)^{\circ}$ and II by $1.01(3)^{\circ}$ with *ac*. The dihedral angle between I and II is $5.04(4)^{\circ}$. In general, the shortest intermolecular contacts are between molecules in adjacent columns with the shortest of these involving the O atoms ($O(2)\cdots H(C8)$ (related by $x-5, y-5, z-5$) $2.44(4)$ Å; $O(2)'\cdots O(2)'$ ($-x, 1-y, 1-z$) $2.685(5)$ Å).

There are no close S \cdots O intermolecular contacts. The S(5) \cdots O(1) intramolecular contacts are $2.749(3)$ Å and $2.804(3)$ Å for I and II, respectively, and are considerably shorter than the sum of their van der Waals' radii (3.15 - 3.25 Å, Bondi, [29]), but slightly longer than those observed in 1,6-dinitro-3,8-trifluoromethylthianthrene ($2.722(9)$ and $2.722(9)$ Å, Dahm, May, D'Amico, Tung and Fuhrhop [30]). In order to maximize the interaction of the O atom with a σ^* orbital (S-C(5a)), the O-S-C(5a) angle should be close to 180° ; while the measured angles are $155.5(1)^{\circ}$ and $155.1(1)^{\circ}$ for I and II, respectively. Although there is a very slight difference in the S(5)-C distances in both I and II, this could be the result of electrostatic effects due to aza and nitro ring substitution.

There are only minor differences in the bond lengths and angles of the two molecules. The only significant differences are the molecular dihedral angles and the dihedral angles between the pyridine rings and the nitro groups of the two molecules. The observation of crystallographically distinct molecules with differing dihedral angles is not uncommon in thianthrenes and has been observed for thianthrene tetraoxide [31] and 1,4-diazathianthrene [32]. Thianthrenes fold along the S-S intramolecular axis and small changes in the C-S-C and C-C-S angles can affect the magnitude of the dihedral angle. Since small angular distortions are generally low energy processes, it is not surprising that crystal packing forces can often influence the dihedral angle in these heterocyclic systems.

It has been observed in phenoxathiins that annular aza substitution results in a flattening (increasing the dihedral angle) of the molecule [33]. Annular aza substitution results in an increase in the dihedral angle of thianthrenes as well. The dihedral angles of I and II (135.00 and 132.52° , respectively) are greater than the $128.28(7)^{\circ}$ found for thianthrene and close to that observed for 1-azathianthrene ($132.13(6)^{\circ}$) [34]. Additionally, 1,4-diazathianthrene has dihedral angles of $137.00(7)^{\circ}$ and $138.93(7)^{\circ}$

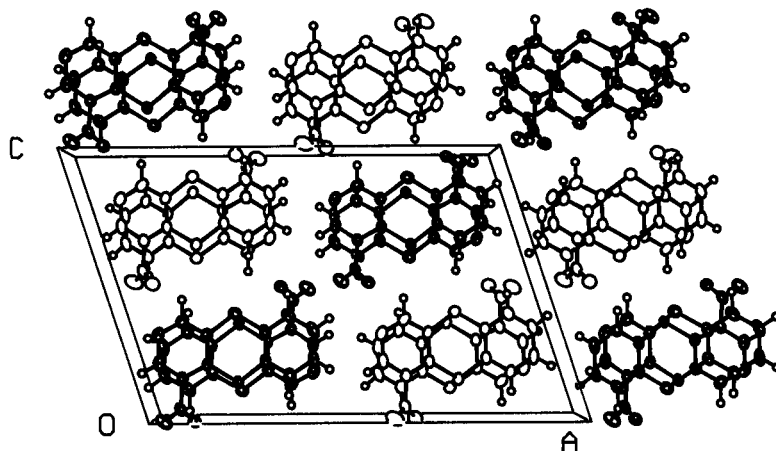


Figure 3. Molecular packing diagram for 4-nitro-2-azathianthrene. Dashed ellipsoids are for atoms of molecule II.

[32] and benzo(*b*)-1,4-diazathianthrene has a dihedral angle of $136.83(10)^\circ$ [35] while dibenzo[*b,i*]-1,4,6,9-tetraazathianthrene [36] and 1,4,6,9-tetraazathianthrene [37] are planar. The planarity of the latter two compounds is surprising because of the large change in the dihedral angle when compared to the other azathianthrenes.

Conclusions.

The synthesis of the sought after 2-azathianthrene has been achieved although it was not possible to prepare the compound by direct condensation in the manner used successfully to prepare the isosterically related 3-azaphenoxathiin [5]. It was instead necessary to condense 3-chloro-4-nitropyridine 1-oxide with the dianion followed by reduction to obtain the parent 2-azathianthrene system **3**. Curiously, direct condensation of 4-chloro-3,5-dinitropyridine with the dianion gave the corresponding 4-nitro-2-azathianthrene (**7**) in good yield. While no explanation may be readily advanced for the failure of the former reaction, it is possible that the occurrence of an intramolecular sulfur-nitro group oxygen interaction may have in some way promoted the latter reaction; tangential support for this contention is offered by the observation of this type of strong, non-bonded interaction in the crystal structure of **7**.

EXPERIMENTAL

Melting points were determined either in open capillary tubes in a Thomas-Hoover melting point apparatus or between glass coverslips on a hot stage apparatus. Infrared spectra were obtained as potassium bromide pellets using a Perkin-Elmer model 283 spectrophotometer unless otherwise indicated. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Proton and carbon nmr spectra were obtained at observation frequencies of 100.060 or 25.158 MHz using Varian XL-100-15 spectrometers operating in the Fourier transform mode and equipped variously with a Varian Model 620-L or Nicolet 1180 computer. Typical instrument parameters were: 90° pulse length = 21 μ sec with a 12 μ sec pulse used for data accumulation; interpulse delays ranged from 3-8 sec; spectral width = ± 2.5 KHz; digitization with 16K points gave an acquisition time of 1.63 sec, the data processed with a 1 Hz apodization prior to Fourier transformation. The spin-lattice (T_1) relaxation time measurements were made using the inversion-recovery sequence [25,26] with a series of fourteen τ values ranging in duration from 0.00025 to 8 seconds with an interpulse delay of 20 seconds. The data was processed using the three parameter fitting program of Kowalewski and co-workers [27].

Synthesis of 3-Chloro-4-nitropyridine 1-Oxide (**4**).

To a solution of 26.11 g (0.23 mole) of 3-chloropyridine in 150 ml of acetic anhydride maintained below 0° 150 ml of 30% hydrogen peroxide (chilled dropping funnel) was slowly added. After the completion of the addition, the reaction mixture was allowed to warm to room temperature at which it was stirred for 5 hours after which it was heated at reflux temperature for 30 hours. The reaction mixture was then allowed to cool and was carefully poured into 200 ml of distilled water. Removal of the solvent *in vacuo* gave a reddish oil which was immediately nitrated without any further purification using a mixture of concentrated sulfuric acid (50 ml) and 30% oleum (20 ml) in 150 ml of fuming nitric acid with refluxing for 4 hours. After cooling, the mixture was poured into 300 ml of ice cold distilled water, the resultant aqueous solution made basic (pH \approx 9) by the

addition of ammonium hydroxide solution. Extraction of the basic aqueous solution with 5×50 ml of dichloromethane followed by drying over magnesium sulfate and concentration gave a yellow crystalline solid in 81% yield, mp 113-114 $^\circ$ (lit mp 113-114 $^\circ$ [10]).

Synthesis of 2-Azathianthrene 2-Oxide (**5**).

To a flame dried flask fitted with a reflux condenser, drying tube and a dry argon purge was added 15 ml of freshly distilled *N,N*-dimethylformamide in which 0.5 g (0.02 mole) of sodium hydride was suspended. To this suspension was added 0.008 mole of benzene-1,2-dithiol, after which the mixture was stirred until hydrogen evolution had abated. An addition of 1.39 g (0.008 mole) of 3-chloro-4-nitropyridine 1-oxide was made to the solution of the dianion, after which the mixture was brought to reflux temperature for 10 hours. Upon cooling, the reaction mixture was poured into 100 ml of distilled water which was extracted with 3×30 ml of chloroform. The combined extracts were back extracted 2×20 ml of 1M sodium carbonate followed by 2×20 ml of distilled water before being dried over magnesium sulfate. Analysis of the crude reaction product by tlc showed two materials to be present, of which the desired 2-azathianthrene 2-oxide (**5**) was the major product. Chromatography over silica using chloroform/methanol (95:5) gave **5** in 89% yield after recrystallization from chloroform, mp 191-192 $^\circ$. The minor product appeared to be a diazathianthrene [39].

The major compound **5** was characterized by $^1\text{H-nmr}$ (deuteriochloroform) $\delta = 8.22$ (d, 1H), 8.00 (dd, 1H), 7.50-7.20 (m, 5H); and $^{13}\text{C-nmr}$ $\delta = 137.76, 137.18, 135.69, 134.84, 133.71, 132.34, 129.45, 129.01, 128.71, 124.07$. The compound gave a molecular ion as the base peak in the electron impact mass spectrum, $m/z = 233$ (100%), 217 (42), 216 (25), 190 (35), 185 (20), 177 (24), 172 (21).

Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{NOS}_2$: C, 56.65; H, 3.00; N, 6.00. Found: C, 56.69; H, 2.85; N, 5.79.

Reduction of 2-Azathianthrene 2-Oxide (**5**) to 2-Azathianthrene (**2**).

To a solution of 1.00 g (0.0043 mole) of **5** in 15 ml of dry chloroform was added 1 ml of freshly distilled phosphorus trichloride as in the procedure of Ochai [8]. The resultant solution was refluxed for 6 hours, cooled and poured into 80 ml of distilled water, after which the biphasic solution was neutralized by the addition of 5M sodium hydroxide. The mixture was extracted with 3×25 ml of chloroform and then dried over magnesium sulfate and concentrated under reduced pressure to yield an off white solid which was purified using flash column chromatography over silica (methanol:chloroform, 2:98) to afford pure 2-azathianthrene (**3**) in 76% yield, mp 85-86 $^\circ$.

The $^1\text{H-nmr}$ spectrum (deuteriochloroform) gave: $\delta = 8.53$ (s, 1H), 8.24 (d, 1H), 7.50-7.10 (m, 5H); analysis of the $^{13}\text{C-nmr}$ spectrum is discussed above. The electron impact mass spectrum again gave the molecular ion as the base peak $m/z = 217$ (100%), 218 (15), 216 (15), 190 (31), 185 (21), 173 (16).

Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{NS}_2$: C, 60.83; H, 3.22; N, 6.45. Found: C, 60.53; H, 3.09; N, 6.19.

Synthesis of 7- and 8-Methyl-2-azathianthrene 2-Oxides.

The synthesis and isolation of 7- and 8-methyl-2-azathianthrene 2-oxides was conducted in a manner identical to that employed in the preparation of 2-azathianthrene 2-oxide (**5**) except that an equivalent amount of toluene-3,4-dithiol was used instead of the benzene-1,2-dithiol employed in the above procedure. Recrystallization from dichloromethane gave a 95% yield of the isomer mixture which resisted all attempts to purify it by chromatographic means, mp 123-125 $^\circ$.

The confirmation of the structure of the isolated material was, however provided by the physical data; $^1\text{H-nmr}$ (deuteriochloroform): $\delta = 8.2$ (s, 1H), 8.0 (d, 4H), 7.3-7.0 (m, 4H), 2.28 (s, 3H); the molecular ion was again the base peak in the electron impact mass spectrum, $m/z = 247$ (100%), 231 (30), 230 (14), 217 (13), 215 (12), 204 (18), 198 (16), 186 (14).

Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{NOS}_2$: C, 58.29; H, 3.64; N, 5.66. Found: C, 58.10; H, 3.68; N, 5.53.

Synthesis of 7- and 8-Methyl-2-azathianthrene.

The procedure employed in the reduction of the methyl-2-azathianthrene 2-oxides mixture to the corresponding methyl analogs of the parent system was identical to the procedure described above for **3**. The product obtained in this case was obtained in an 88% yield following recrystallization from diethyl ether. Once again, the mixture resisted all attempts to separate it chromatographically. ¹H-nmr (deuteriochloroform): $\delta = 8.5$ (s, 1H), 8.3 (d, 1H), 7.3-7.1 (m, 3H), 7.0 (d, 1H), 2.23 (s, 3H); the molecular ion was the base peak in the electron impact mass spectrum, $m/z = 231$ (100%), 232 (15), 204 (19), 203 (18), 199 (17), 198 (45), 102 (13).

Anal. Calcd. for C₁₂H₉NS₂: C, 62.34; H, 3.89; N, 6.06. *Found:* C, 62.41; H, 3.59; N, 5.67.

Synthesis of 4-Chloro-3,5-dinitropyridine (6).

4-Chloro-3,5-dinitropyridine was prepared according to the procedure of Okafor [38]. To a cooled (0°) and well stirred mixture of fuming nitric acid (22.5 ml) and 30% oleum (20 ml) was added 1.4 g (0.01 mole) 4-hydroxy-3-nitropyridine at a rate such that the temperature never exceeded 50°. The reaction mixture was then stirred at 100° for 24 hours and then at 140° for an additional 24 hours. The reaction mixture was then cooled and poured carefully onto ice before being partially neutralized with concentrated ammonium hydroxide. The product was precipitated during the neutralization process, collected by filtration and recrystallized from hot water to give 1.6 g (90% yield), mp ~ 300° (physical properties were identical to those reported by Okafor [38]). The 3,5-dinitro-4-hydroxypyridine was converted to the chloro compound by reacting 1.85 g (0.01 mole) with 3.8 g phosphorus pentachloride in 5 ml of phosphorus oxychloride heated at reflux temperature for 3 hours. The phosphorus halides were removed by distillation leaving a dark residue which was boiled with 250 ml of ethyl acetate. The ethyl acetate solution was back extracted with 2 x 100 ml of distilled water and dried over sodium sulfate. Upon removal of the solvent *in vacuo* a brown solid, 1.6 g (79% yield) was obtained, mp 237-238° (lit. mp 236-239°) which was used without any further purification.

Synthesis of 4-Nitro-2-azathianthrene (7).

To a stirred solution of 0.5 g (0.0035 mole) of the dianion of benzene-1,2-dithiol, prepared as described above, in 15 ml of dry, freshly distilled *N,N*-dimethylformamide was added a solution of 0.72 g (0.0035 mole) of 4-chloro-3,5-dinitropyridine in 5 ml of dry, freshly distilled *N,N*-dimethylformamide, the entire system maintained under a dry argon purge. The reaction mixture was stirred at room temperature for six hours and then poured into 150 ml of distilled water. The aqueous mixture was extracted with 2 x 100 ml portions of chloroform after which the combined extracts were back extracted with 2 x 100 ml portions of distilled water. Following drying over sodium sulfate, the chloroform was removed *in vacuo* to give a solid which recrystallized from chloroform to afford 0.85 g (92% yield) of 4-nitro-2-azathianthrene, mp 191-192°; ¹H-nmr (deuteriochloroform): $\delta = 9.10$ (s, 1H), 8.71 (s, 1H), 7.5-7.3 (m, 4H); ¹³C-nmr: δ (T, sec) (* = may be permuted), 150.77 (4.04, C1), 145.52 (-, C4), 144.14 (1.86, C3), 137.08 (-, C β), 132.50 (-, C α'), 131.64 (*-, C β'), 131.63 (*-, C α), 129.27 (2.39, C6 or C9), 129.07 (1.98, C7 and C8), 128.50 (2.69, C6 or C9). The electron impact mass spectrum gave a strong molecular ion, $m/z = 262$ (45%), 263 (8), 264 (5), 216 (25), 189 (38), 184 (20), 177 (20), 172 (30), 171 (20), 146 (20), 145 (100).

Anal. Calcd. for C₁₁H₆N₂O₂S₂: C, 50.37; H, 2.31; N, 10.68. *Found:* C, 50.46; H, 2.33; N, 10.66.

X-Ray Crystallography of 4-Nitro-2-azathianthrene (7).

A yellow needle, 0.16 mm x 0.18 mm x 0.61 mm, was obtained by slow evaporation from chloroform. The molecule crystallized in the P2₁/n space group, $a = 20.712(3)$, $b = 7.8109(13)$, $c = 13.720(2)$ Å, $\beta = 107.880(11)^\circ$, $V = 2112.4(6)$ Å³, $Z = 8$, $D_c = 1.65$ g/cm³ (163°K), MoK α radiation, $\lambda = 0.71069$ Å, $\mu = 4.71$ cm⁻¹. A Syntex P2, diffractometer equipped with a graphite monochromator, and a Syntex LT-1, low tem-

perature (163°K) delivery system was employed for the study. Lattice parameters from least-squares refinement of the setting angles of 45 reflections with $20.6^\circ < 2\theta < 31.0^\circ$. Omega scan technique, 4826 unique reflections, 2θ from 4° to 55° , scan range of $1^\circ \omega$, scan rate from 3° to 6° /minute, (only unique data with ranges; $h = 0 - 26$, $k = 0 - 10$, $l = -17 - 16$). Four reflections (1,2,1; -6,0,0; 0,0,-6; -1,-2,-1) remeasured after every 96 reflections. Data corrected for Lp effects, but not absorption nor decay. Data reduction was performed as described by Riley and Davis [40]. Reflections with $F_o < 4\sigma(F_o)$ were considered unobserved (1765 reflections). The structure of the molecule was solved using MULTAN78 [41] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for the non-H atoms. H atoms were located from a difference map and were refined with isotropic thermal parameters. Function minimized $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$ and $\sigma(F_o) = .5(kl)^{-1/2}[(s(1))^2 + (.041)^2]^{1/2}$. Intensity, I, given by $(I_{peak} - I_{background})^*$ (scan rate), 0.04 is a factor used to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects. Sigma(I) estimated from counting statistics is given by, $\sigma(I) = [(I_{peak} + I_{background})^{1/2} * (\text{scan rate})]$. The final R = 0.051 for 3061 reflections, 355 parameters, $wR = .053$ ($R_{int} = .090$, $wR_{int} = .059$), goodness of fit = 1.39. Maximum $\Delta I/\sigma I = .013$ in the final refinement cycle, minimum and maximum peaks in final difference map are $-.35$ and $.71 e^{-1} \text{Å}^{-3}$, respectively. Scattering factors for the non-H atoms were taken from Cromer and Mann [42] with anomalous-dispersion corrections from Cromer and Liberman [43], while scattering factors for H atoms from Stewart, Davidson and Simpson [44]; linear absorption coefficients were taken from International Tables for X-ray Crystallography [45]. The least-squares planes program was supplied by Cordes [46]; other computer programs from reference 11 of Gadol and Davis [47].

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