Chemistry of the Phenoxathiins and Isosterically Related Heterocycles. XXIII (1). 1-Azathianthrene: First Reported Synthesis of a Monoazathianthrene and the Investigation of the ^{13}C-NMR Spectrum Using Two-dimensional NMR Techniques

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The reaction of the dianion of 3-mercaptopyridin-2(1*H*)-thione with 2-chloronitrobenzene in *N,N*-dimethylformamide leads to the formation of 1-azathianthrene, the first reported mono-aza analog of the thianthrene ring system. A partial assignment of the ^{13}C-nmr spectrum of the title compound is reported, the assignment based on chemical shift arguments, spin-lattice (T_1) relaxation times and ^{1}H-^{13}C spin coupling constants. Amplitude modulated two-dimensional Fourier transform (AM2DFT) techniques were employed for the acquisition of the heteronuclear spin-coupling constants.

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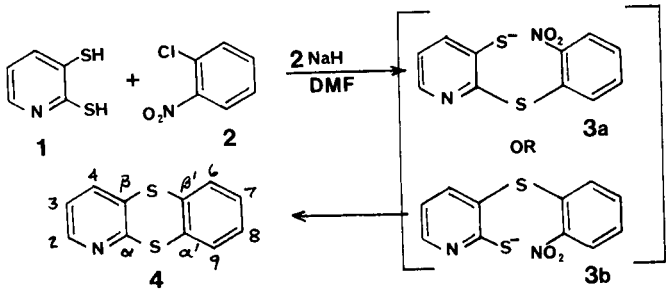
Introduction

The syntheses of all four possible monoazaphenothiazines and monoazaphenoxazines have been reported and are discussed in several recent reviews (3). Recent reports have also detailed the syntheses of all four of the monoazaphenoxathiin (4-7) ring systems. However, although various examples of the diazathianthrene (8-11) and tetraazathianthrene (12-14) ring systems are known, there have been no reported syntheses of either of the two possible monoazathianthrene systems. In light of the recently reported correlation between the ^{13}C-nmr chemical shift of the Cα resonance and the molecular dihedral in a series of phenoxathiin analogs (15), we were prompted to extend out investigations to include the 1-azathianthrene (4) ring system. This synthesis was undertaken with the ultimate specific intent of examining the thianthrene ring system for the effects of annular aza-substitution on the molecular dihedral angle.

SCHEME I



Synthesis and Characterization of 1-Azathianthrene.

For the synthesis of the 1-azathianthrene ring system, we utilized 3-mercaptopyridin-2(1*H*)-thione (**1**) (16) as a precursor. To a chilled and well stirred suspension of sodium hydride in *N,N*-dimethylformamide (DMF) was added a solution of **1** in a small volume of DMF. To this solution, after the evolution of hydrogen had ceased, was added a chilled solution of 2-chloronitrobenzene (**2**) (Scheme I). The reaction mixture was then slowly allowed to come to room temperature for the period of one hour, the reaction was then brought to reflux for six hours, cooled and poured into chilled distilled water. The resultant aqueous DMF solution was then extracted repetitively with ethyl acetate, and the combined extracts back extracted with 10% sodium carbonate followed by distilled water, and the final organic solution dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude reaction product was redissolved in acetone and adsorbed onto a minimal quantity of silica. The acetone was removed *in vacuo* and the dry silica slurried onto a prepared column in cyclohexane. The column was eluted with a linear gradient solvent system which was taken from pure cyclohexane to a mixture of cyclohexane:ethyl acetate (3:7), giving **4** in pure form. Recrystallization of **4** from hexanes gave the compound as fine, slightly yellowish needles, mp 109-110°, in a 45% yield. Examination of the low resolution mass spectrum of **4** showed the presence of an intense molecular ion, M^+ = 217 (100%), the molecular cluster consistent with the anticipated elemental composition

$C_{10}H_7NS_2$. The high resolution mass spectrum was also obtained, M^+ calculated = 217.0019; found = 217.0019. The proton nmr spectrum of **4**, obtained at 200 MHz showed the protons of the pyridine portion of the molecule as a simple and well resolved ABX spin system. In contrast, the four protons of the benzene portion of the molecule comprised an AA'BB' spin system which gave rise to a complex multipet centered from 7.00-7.25 ppm. No effort was made to interpret or to simulate this spin system.

^{13}C-NMR Spectrum of 1-Azathianthrene (**4**).

The eleven carbon resonances in the ^{1}H-decoupled ^{13}C-nmr spectrum of **4** were resolved at 25.2 MHz (Figure 1). The assignment of the protonated carbon resonances of

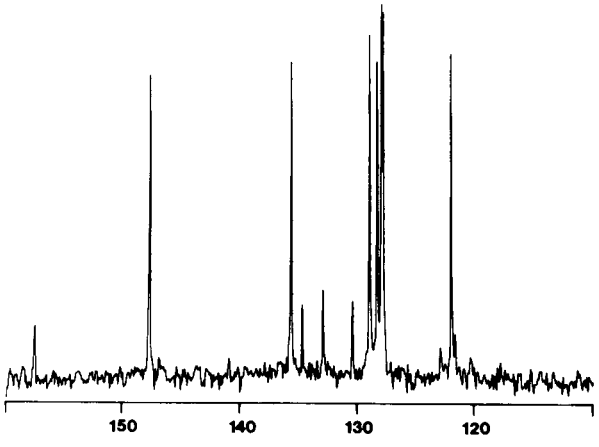


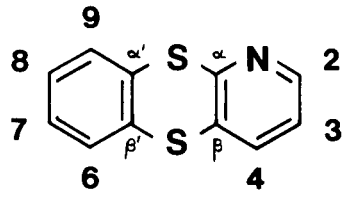
Figure 1. ^{1}H-Decoupled ^{13}C-nmr spectrum of 1-azathianthrene (**4**) in deuteriochloroform at 25.2 MHz.

the pyridine portion of the molecule was straight-forward, based on a comparison with the chemical shifts of 1,6-diazathianthrene (11). The Cα quarternary carbon resonance was also assigned on the basis of chemical shift. The remaining quaternary carbons, a pool of three resonances, could not however be assigned at this time. The protonated carbons of the benzene portion of the molecule likewise presented a substantial assignment problem, as there is no justifiable basis for making the assignments of these resonances from chemical shift data alone.

Spin-lattice (T_1) relaxation times were measured for **4** using the inversion-recovery technique on a sample which was prepared by dissolving 250 mg of **4** in 3.0 ml of deuteriochloroform. The sample was rigorously degassed prior to the study. By analogy with recent studies of the pyrrolo[3,2,1-*kl*]phenothiazine (17), benzo[*b*]-1,4,9-triazaphenoxathiin (18) and several phenarsazine analogs (19), there should be an axis of anisotropic reorientation passing lengthwise through the molecular framework, as shown by **5**. The assigned resonances of the pyridine protion of the molecule should provide an internal check on this mode of reorientation. Thus, the protonated carbons of the pyr-

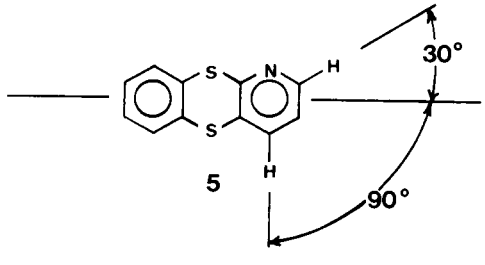
Table I

Calculated *vs.* Observed 25.2 MHz ^{13}C-NMR Chemical Shifts and Spin-lattice (T_1) Relaxation Times for 1-Azathianthrene (**4**) in Deuteriochloroform



Carbon	δ^{13}C calculated (a)	observed	$\Delta\delta$	T_1 (sec)
α	153.5	157.65	+ 4.2	—
β	128.4	130.46	+ 2.1	—
α' (b)	—	134.79	—	—
β' (b)	—	133.01	—	—
2	148.1	147.82	− 0.3	3.0
3	122.9	122.00	− 0.9	2.8
4	136.4	135.74	− 0.7	4.0
6 (c)	—	128.99	—	4.0
7 (d)	—	127.97	—	2.9
8 (d)	—	127.83	—	3.0
9 (c)	—	128.35	—	3.9

(a) Chemical shift calculations were obtained for 4 by incrementation of the ^{13}C-nmr shifts of thianthrene for annular aza-insertion as previously described *cf.* references 5 and 6. (b), (c), (d) Possibly permuted pairs of assignments.



idine ring should have C-H bond vectors oriented at approximately 30° to the axis of anisotropic reorientation for C2 and C3, while the C4 C-H bond vector should be oriented at about 90° to the axis. This is indeed consistent with the observed relaxation times of 3.0, 2.8 and 4.0 seconds, respectively. The four protonated carbon atoms of the benzene portion of the molecule which exhibited chemical shifts of δ = 128.99, 128.35, 127.97 and 127.83 had relaxation times of 4.0, 3.9, 2.9 and 3.0 seconds, respectively (Table I). These relaxation times, which are clearly consis-

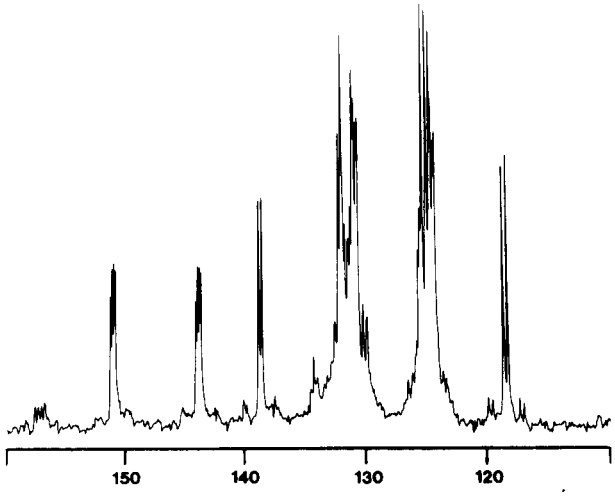


Figure 2. ^{1}H-^{13}C Spin-coupled nmr spectrum of 1-azathianthrene (**4**) in deuteriochloroform at 25.2 MHz.

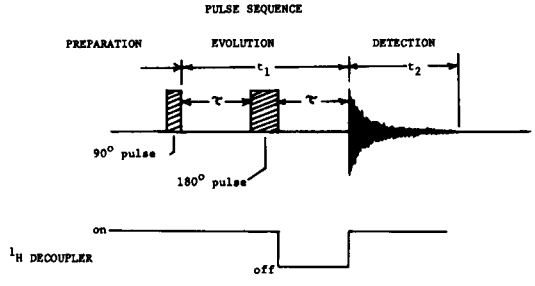


Figure 3. Schematic representation of the sequence of events transpiring during the execution of an amplitude modulate two-dimensional nmr experiment.

Table II

^{1}H-^{13}C Spin-coupling Constants of 1-Azathianthrene (**4**) in Deuteriochloroform Obtained from the Amplitude Modulated Two-dimensional Fourier transform NMR Experiment. Couplings are given as J rather than as J/2 as obtained directly from the two dimensional nmr experiment.

Carbon	^{1}H-^{13}C Coupling Constants (Hz) $^{1}J_{CH}$	$^{2}J_{CH}$	$^{3}J_{CH}$
α	—	—	$J_{C_\alpha H_2} = 13.2$
	—	—	$J_{C_\alpha H_4} = 6.1$
β	—	$J_{C_\beta H_4} = 2.3$	$J_{C_\beta H_3} = 7.2$
α' (a)	—	—	$J_{C_{\alpha'} H_6} = 7.7$
	—	—	$J_{C_{\alpha'} H_8} = 7.7$
β' (a)	—	—	$J_{C_{\beta'} H_7} = 7.6$
	—	—	$J_{C_{\beta'} H_9} = 7.6$
2	$J_{C_2H_2} = 184.3$	$J_{C_2H_3} = 3.8$	$J_{C_2H_4} = 8.6$
3	$J_{C_3H_3} = 166.5$	$J_{C_3H_2} = 8.9$	—
4	$J_{C_4H_4} = 167.2$	—	$J_{C_4H_2} = 7.0$
6 (b)	$J_{C_6H_6} = 164.3$	$J_{C_6H_7} = 3.3$	$J_{C_6H_8} = 6.6$
7 (c)	$J_{C_7H_7} = 163.2$	—	$J_{C_7H_9} = 8.5$
8 (c)	$J_{C_8H_8} = 163.2$	—	$J_{C_8H_6} = 8.6$
9 (b)	$J_{C_9H_9} = 162.2$	$J_{C_9H_8} = 2.4$	$J_{C_9H_7} = 6.6$

(a) (b) (c). Possibly permuted pairs of assignments.

tent with the angular orientations of the C-H bond vectors illustrated by **5**, allowed the subgrouping of the protonated resonances from the benzene derived portion of the molecule. Thus, C6 and C9 were assigned to the resonances at δ = 128.99 and 128.35 while the C7 and C8 carbon atoms were assigned to the resonances observed at δ = 127.97 and 127.83. Beyond this, however, no further assignments could be made within the individual subgroups.

The ^{1}H-^{13}C spin-coupled spectrum of **4**, which was obtained using conventional gated decoupling techniques, was also examined and is shown in Figure 2. It proved to be extremely complex. Attempts to simplify the spectrum by utilization of selective excitation techniques (20-22) were not successful because of the need to obtain very fine resolution during the excitation. This consideration precluded the utilization of sufficient numbers of attenuated pulses to obtain the requisite resolution (23). Thus, an amplitude modulated two-dimensional Fourier transform (AM2DFT) experiment was conducted in the hope of resolving all of the coupled signals so that a final assignment could be made.

The AM2DFT nmr experiment is a simple modification of the spin-echo technique which was originally described by Hahn and Maxwell (24). The sequence of events occuring in the spectrometer during the execution of the experiment is shown schematically in Figure 3, a gating of the ^{1}H-decoupler superimposed over the generation of the spin-echo. The execution of a single such experiment gives rise to a data set which it is convenient to denote $S(t_1,t_2)$ (the time periods represented here, t_1, t_2, not to be confused with the relaxation times T_1 and T_2). Systematic incrementation of the t_1 interval, (256 incrementations utilized in this case) thus provides a data set in which chemical shift infomation is contained in F_2 (obtained by the first Fourier transformation of the t_2 interval) and spin coupling data in the F_1 domain (obtained by the second Fourier transformation with respect to t_1) (25).

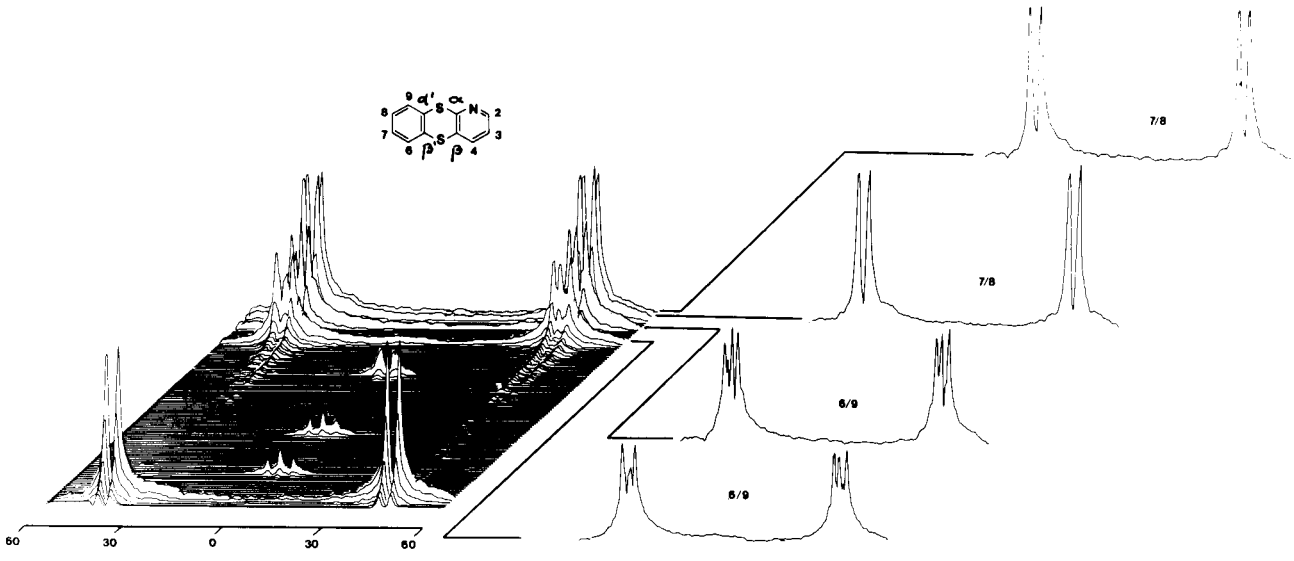


Figure 4. White-washed stackplot of the $S(F_2,F_1)$ data file from the amplitude modulated two-dimensional ^{13}C-nmr spectrum of 1-azathianthrene (**4**) in deuteriochloroform. Individual sub-spectra of the protonated benzenoid carbons are shown to the right.

A useful presentation of the data from the AM2DFT nmr experiment performed on 1-azathianthrene (**4**) is obtianed by plotting the $S(F_2,F_1)$ data array. The "white -washed" stackplot of the $S(F_2,F_1)$ spectrum is shown in Figure 4, spin-coupling information shown horizontally while chemical shift information is displayed along the vertical F_2 axis. Examination of the appropriate individual $S(F_2,F_1)$ data files, shown to the right in Figure 4, provided unambiguous spin-coupling data for all of the resonances contained in the spectrum of **4**. These data are summarized in Table II and it should be noted that this information is obtained despite the complexity of the conventional gated decoupled spectrum whcih is shown in Figure 2. Unfortunately, despite the availability of unequivocal spin-coupling information, an assignment of the protonated ^{13}C-resonances of **4** could not be accomplished. It was however, possible to unequivocally assign one additional quaternary carbon on the basis of the AM2DFT experiment. In particular, the Cβ resonance, which would be expected to exhibit a relatively large three-bond coupling and a somewhat smaller two-bond coupling, was unequivocally assignable to the resonance observed at δ = 130.46. Assignment of the remaining Cα' and Cβ' quaternary resonances, like the protonated resonances from the benzene portion of the molecule, could not be completed solely on the basis of the spin-coupling constant formation provided by the AM2DFT experiment.

Mechanistic Considerations.

In addition to the aforementioned problems encountered with the total assignment of the ^{13}C-nmr spectrum of **4**, mechanistically interesting questions may also be posed with regard to the reaction pathway leading to the formation of 4 (Scheme I).

While it has been rigorously shown that the 2-thiolate anion of 3-hydroxypyridine-2(1*H*)-thione is the stronger of the two nucleophilic species in the synthesis of 1-azaphenoxathiin (4) and its substituted analogs (26), a somewhat different situation arises in the synthesis of 1-azathianthrene (**4**). Here, the two nucleophilic species to be compared are both thiolates and one must consider the relative importance of the 2-thiolate being able to exist in the corresponding thione form as well as the potential consequences of this tautomeric equilibrium on the relative nucleophilicity. The contention that the 2-thiolate exists predominantly in the thione form is supported by a recent study of pyridinethiols reported by Stefanik (27). This study found that pyridine-2-thiol, in solution, exists predominantly in the thione form to the extent of 95 ± 5%. The 3-thiol, in contrast, was found to exist predominantly as the thiol rather than as the corresponding betaine. Based on this observation, it is plausible to suggest that it may be the 3-thiolate anion which is responsible for the nucleophilic attack in reactions employing the dianion of 3-mercaptopyridin-2(1*H*)-thione. If indeed that is the case, it would allow at least some control over product composition in reactions leading to substituted 1-azathianthrenes barring the occurrence of a Smiles rearrangement which cannot be ruled out in this system. Further studies in this area are at present underway and will be forthcoming.

EXPERIMENTAL

All solvents utilized were freshly distilled prior to use and were stored over 3 Å Linde molecular sieves with the exception of the *N,N*-dimethylformamide which was distilled from calcium hydride powder immediately prior to use. Melting points were obtained in open capillary tubes in a Thomas-Hoover melting point apparatus and are reported uncorrected. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrophotometer as potassium bromide pellets. The ^{1}H-nmr spectra were recorded on a Nicolet NT-200 spectrometer operating at 200.068 MHz in the Fourier transform mode using the following parameters: pulse width = 5 μ sec (7.9 μ sec = 90° pulse); interpulse delay = acquisition time; spectra were obtained using a spectral width of ± 1.2 KHz with 32K data points (16K after Fourier transform to give an acquisition time of 6.82 sec). The ^{13}C-nmr spectra were obtained on a Varian XL-100-15 spectrometer operating at 25.158 MHz in the Fourier transform mode and equipped with a Nicolet NIC-1180 computer interfaced through a Model 293A' pulse programmer. Conventional ^{1}H-decoupled ^{13}C and ^{1}H-^{13}C spin-coupled spectra were obtained using the following instrument parameters: pulse width = 12 μ sec (21 μ sec = 90° pulse); interpulse delay = 8 sec; spectral width = ± 2.5 KHz; decoupled spectra were obtained using 16K data points with an acquisition time of 1.63 sec; apodization = 0.5 sec.

The amplitude modulated two-dimensional Fourier transform (AM2DFT) ^{13}C-nmr experiment was conducted using the standard Nicolet operating software implemented *via* the 293A' pulse programmer. The 90° and 180° pulses were set at 21 and 42 μ sec respectively and the individual spectra comprising the initial $S(t_1,t_2)$ data set were acquired with a spectral width of ± 600 Hz using 1K data points which gave a digital resolution of 1.17 Hz in the F_2 dimension after transformation. The complete $S(t_1,t_2)$ data set consisted of 256 incremented values of t_1 with an increment of 4.167 μ sec which gave spectral window of ± 60 Hz in the F_1 dimension after completion of the second Fourier transformation, giving a digital resolution of 0.47 Hz. All AM2DFT data shown in Figure 4 was apodized in the usual fashion using a 0.5 sec time constant applied in both transformations, the data subjected to magnitude calculation following the second Fourier transform to give the absolute value spectrum. All coupling constants shown in Table II are given at their true J rather than as J/2 as obtained from the examination of the individual traces of the $S(F_2,F_1)$ data files.

Synthesis of 1-Azathianthrene (**4**).

To a carefully dried three neck flask fitted with a reflux condenser and a dry argon purge was added 20 ml of freshly distilled DMF in which 0.144 g (6 mmoles) of 99% sodium hydride was suspended. To the stirred suspension was added 0.430 g (3 mmoles) of 3 mercaptopyridine-2(1*H*)-thione (**1**), after which the mixture was stirred overnight. The resultant disodium salt was only partially soluble in the DMF and to this stirred suspension was added 0.473 g (3 mmoles) of *o*-chloronitrobenzene in 20 ml of DMF, the addition conducted over a period of 20 minutes. Upon completion of the addition, the reaction mixture was stirred at room temperature for one additional hour and was then brought to reflux for six hours. After completion of the reflux period, the reaction was allowed to cool and was then poured into 200 ml of chilled distilled water. The resultant aqueous-DMF mixture was then extracted with 3 × 150 ml of ethyl acetate, the combined ethyl acetate extracts were back extracted with 2 × 50 ml of 10% sodium carbonate followed by 2 × 100 ml extractions with distilled water. The final ethyl acetate solution was then dried over anhydrous sodium sulfate and the solvent removed under reduced pressure.

Purification of the crude reaction product was accomplished by linear gradient elution over silica using a gradient which was varied from pure cyclohexane to a mixture of cyclohexane:ethyl acetate (3:7). The 1-azathianthrene (**4**) obtained by this method was recrystallized from hexanes to give fine, slightly yellowish-white crystals, mp 109-110°, 0.296 g (45% yield); ir: ν (cm^{-1}) 3030, 1540, 1445, 1425, 1385, 1370, 1245, 1140, 1105, 790, 750, 725. ms: M^+ (% relative intensity) M^+ = 217 (100), M + 1 = 218 (15.2), M + 2 = 219 (10.1). M + 3 = 220 (1.2), M^+-HCN = 200 (3.5), M^+-S = 185 (29.9). M^+-CS = 173 (41.6), 172 (11.4), 147 (7.5), 140 (10.9). The ^{13}C-nmr chemical shift data as calculated *vs.* observed chemical shift are shown in Table I, accompanied by the spin-lattice (T_1) relaxation times of the protonated carbons which were measured using the inversion-recovery technique; ^{1}H-^{13}C spin-coupling constants are shown in Table II and were obtained from the AM2DFT experiment.

Anal. Calcd. for $C_{11}H_7NS_2$: C, 60.83; H, 3.23; N, 6.45. Found: C, 60.89; H, 3.27; N, 6.40.

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