Chemistry of the Phenoxathiins and Isosterically Related Heterocycles. XXXI [1]. Synthesis of the 1,3-Diazaphenoxathiin Ring System and the Relationship of the ^{13}C-NMR Chemical Shift of the C-10a Resonances to the Molecular Dihedral Angle Determined by X-Ray Diffraction: A Further Investigation

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Synthesis of the 1,3-diazaphenoxathiin ring system and the confirmation of its structure by ^{13}C-nmr spectroscopy and X-ray crystallography are reported. Implications of the ^{13}C-nmr chemical shift of the C-10a resonance and its relationship to the molecular dihedral angle are presented. The molecule crystallizes in the Pbca space group and was found to have a dihedral angle of 165.5(9)°, the structure refining to a final R-factor of T = 0.0427.

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Syntheses of three of the four possible monoazaphenoxathiin parent ring systems have been reported [3-5] as has the synthesis of one analog of the remaining 4-azaphenoxathiin ring system [6]. More recently, the syntheses of the first dipyrido[1,4]oxathiins have been reported [7-9] as have those of several benz[1,4]oxathiinopyridazines [10-12]. There have, however been no reports in the literature of either of the two possible benz[1,4]oxathiinpyrimidines: 1,3-diazaphenoxathiin (**6**) and 2,4-diazaphenoxathiin (**9**). Interestingly, based upon the previously reported correlation between the ^{13}C-nmr chemical shift of the C-10a resonance and the molecular dihedral angle [13,14], considerably different dihedral angles would be expected for these two ring systems (dihedral angles referred to in the case of **6** and **9** are the angles formed by the intersection of the planes containing the benzene and pyrimidine rings contained in the molecule — the sulfur and oxygen atoms are not included in either plane since they are frequently somewhat out of the plane — the dihedral angle referred to is illustrated in Figure 1). Calculated chemical shifts (see Table I) suggest that 1,3-diazaphenoxathiin (**6**) should be relatively planar while 2,4-diazaphenoxathiin (**9**) should be folded to an even greater extent than the parent phenoxathiin ring system as a result of the location of the annular aza-substitutions relative to the 10a position. We now wish to report the synthesis of 1,3-diazaphenoxathiin (**6**), the assignment of the ^{13}C-nmr spectrum and the crystal structure of the molecule.

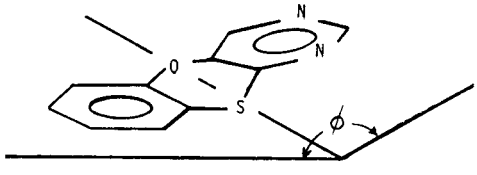
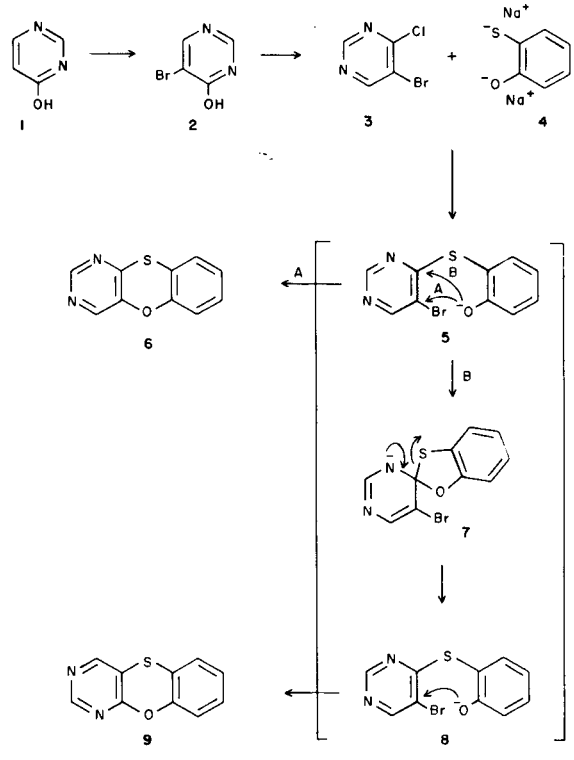


Figure 1. Schematic representation of the molecular dihedral angle in the phenoxathiin system. The dihedral angle is that formed by the intersection of the planes containing the benzene ring and the pyrimidine ring, approximately in the vicinity of the heteroatoms of the central ring which are excluded from the calculated angle (see Table V).

SCHEME I

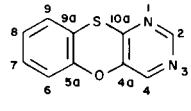


The synthesis of 1,3-diazaphenoxathiin (**6**) was based on the condensation of the disodium salt of *o*-mercaptophenol (**4**) with 5-bromo-4-chloropyrimidine (**3**) (Scheme I). The synthesis of **3** utilized commercially available 4-hydroxypyrimidine (**1**) which was first brominated to afford **2** which on subsequent reaction with phosphoryl chloride gave **3** [15].

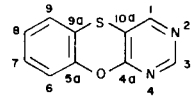
Amongst the problems inherent in the utilization of pyrimidines in the synthesis of more complex heterocycles is the relatively low reactivity of substituents at the 5-position toward nucleophilic displacement. Work in the phenothiazine and phenoxazine series [16] has shown, however, that it is feasible to displace a 5-bromo substituent with either anilino or thiolate species. In general, these reactions have employed refluxing *N,N*-dimethylformamide (DMF) as the solvent with such bases as potassium carbonate. Based upon these observations, we thus elected to attempt the cyclization of **3** with the disodium salt of *o*-mercaptophenol (**4**) in refluxing DMF as shown in Scheme I. Furthermore, since it has recently been shown that Smiles rearrangements may be induced in the phenoxathiin series when suitably substituted reagents are employed [12], the possibility of forming the 2,4-diazaphenoxathiin ring system during the preparation of the 1,3-diaza system must be considered as a viable possibility. Thus, the rearrangement of a suitably substituted analog of the phenolate sulfide intermediate (**5**) could be envisioned to form the spiro-intermediate (pathway B, Scheme I) followed by collapse and cyclization to give **9**. Although we have not, as yet, undertaken the synthesis of 2,4-diazaphenoxathiin or any of its analogs, we include 2,4-diazaphenoxathiin (**9**) in our discussion here because of the potential significance of the calculated ^{13}C-nmr chemical shift of the C-10a resonance of this molecule (see Table I and discussion below).

Table I

Calculated ^{13}C-NMR Chemical Shifts of 1,3-Diazaphenoxathiin (**6**) and 2,4-Diazaphenoxathiin (**9**) *vs.* the Observed ^{13}C-NMR Chemical Shifts of 1,3-Diazaphenoxathiin (**6**) in Deuteriochloroform at 25.158 MHz and a Temperature of 33°



6



9

Position	δ ^{13}C calcd. **6**	**9**	δ ^{13}C obs. **6**	Δδ ^{13}C
1	——	156.0	——	——
2	166.2	——	153.53	−12.7
3	——	168.5	——	——
4	146.1	——	142.71	−3.4
4a	142.3	178.5	146.15	+3.9
5a	149.9	149.9	149.13	−0.8
6	117.5	117.5	117.87	+0.4
7	126.5	126.5	127.22	+0.7
8	124.2	124.2	125.30	+1.1
9	127.4	127.4	128.64	+1.2
9a	119.9	119.9	116.51	−3.4
10a	148.4	109.7	153.85	+5.5

^{13}C-NMR Spectroscopy.

From the calculated ^{13}C-nmr chemical shift data contained in Table I, it can be seen that the two ring systems, **6** and **9**, are expected to give substantially different chemical shifts for their respective quaternary carbons. These differences would consequently allow the convenient differentiation of these two ring systems even if they should happen to be formed in the same reaction. Thus, 1,3-diazaphenoxathiin (**6**), in which the annular nitrogen atoms are located *ortho* and *para* to the sulfur bearing C-10a quaternary position, would be expected to have three quaternary carbons resonating downfield at δ = 148.4, 142.3 and 149.9 for C-10a, C-4a and C-5a respectively. In contrast, a single quaternary carbon, C-9a, would be expected to resonate upfield at δ = 119.9. Relative to the 1,3-diaza-isomer, the quaternary carbon resonances of 2,4-diazaphenoxathiin (**9**) would be expected to present a considerably different arrangement. As is shown in Table I, two resonances would be expected downfield, one very far downfield at δ = 178.5 and the other in a more normal region of the spectrum at δ = 149.9 for C-4a and C5-a respectively. Additionally, two quaternary carbon resonances would be expected to appear upfield at δ = 109.7 and 119.9 for C-10a and C-9a respectively.

As anticipated, the quaternary carbon resonances of **6** were observed at 153.85, 149.13, 146.15 and 116.51 ppm, which is in reasonable accord with the expectations presented above (see Table I) based on the calculated chemical shifts. Protonated carbon resonances contained in the benzene portion of the molecule were assigned on the basis of comparison of the observed chemical shifts with calculated chemical shift data. In contrast, unequivocal assignment of the C-2 and C-4 resonances necessitated the acquisition of a ^{1}H coupled ^{13}C-nmr spectrum. Thus, C-2, situated between two annular nitrogens, was expected to exhibit a one bond coupling ($^{1}J_{CH}$) of approximately 205 Hz as in the corresponding position of pyrimidine itself [17]. In contrast, the C-4 resonance, flanked only by a single annular nitrogen, was expected to exhibit a one bond coupling of approximately 180 Hz [17]. These expectations were substantiated by the coupled spectrum, the resonance at δ = 153.85 exhibiting a coupling $^{1}J_{C_2H_2}$ = 207 Hz while the resonance at 142.71 exhibited a coupling $^{1}J_{C_4H_4}$ = 184.6 Hz, thus allowing the unequivocal assignment of these resonances. The balance of the ^{1}H-^{13}C heteronuclear spin coupling constants of **6** are collected in Table II and are unremarkable.

Table II

^1H- ^{13}C Spin Coupling Constants of the Protonated Carbon Resonances of 1,3-Diazaphenoxathiin (**6**)

Position	$^1J_{CH}$	$^2J_{CH}$	$^3J_{CH}$
2	$J_{C_2H_2}$ = 206.7	——	$J_{C_2H_4}$ = 11.4
4	$J_{C_4H_4}$ = 184.5	——	$J_{C_4H_2}$ = 10.0
6	$J_{C_6H_6}$ = 164.0	$J_{C_6H_7}$ = 1.3	$J_{C_6H_8}$ = 4.2
7	$J_{C_7H_7}$ = 161.5	$J_{C_7H_6}$ or $J_{C_7H_8}$ = 2.5 [a]	$J_{C_7H_9}$ = 7.8
8	$J_{C_8H_8}$ = 164.0	$J_{C_8H_7}$ or $J_{C_8H_9}$ = 2.8 [a]	$J_{C_8H_6}$ = 7.3
9	$J_{C_9H_9}$ = 168.8	$J_{C_9H_8}$ = 3.7	$J_{C_9H_7}$ = 8.8

[a] Coupling could be to either of the protons indicated. No means of unequivocally assigning the coupling is avilable from the proton-coupled carbon spectrum.

Correlation of the ^{13}C-NMR Chemical Shift of the C-10a Resonance With the Molecular Dihedral Angle Determined by X-Ray Crystallography.

Assignment of the C-10a resonance as the signal observed at δ = 153.85 allows the consideration of the interrelation of the ^{13}C-nmr chemical shift of C-10a to the molecular dihedral angle. From previous work [13,14], which has recently been updated on the basis of a redetermination of the dihedral angle of the parent phenoxathiin ring system [18] (ϕ = 147.76), the dihedral angle of **6** may be predicted from the nmr spectral data. Thus, from least squares data [18], the predicted dihedral angle of 1,3-diazaphenoxathiin (**6**) was ϕ = 194.1° (which crystallographically would be measured as the complementary angle of 165.9°). The interpretation of this dihedral angle information, interestingly, leads to the possible conclusion that increasing election withdrawal at the sulfur bearing carbon flattens the molecular framework to planar but that further electron withdrawal begins to refold the system (toward the expected complementary angle of 165.9° in ths case).

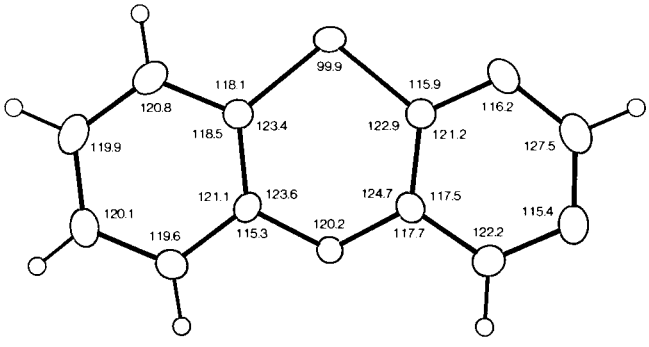


Figure 2. Atom numbering scheme and bond lengths of 1,3-diazaphenoxathiin (**6**).

Table III

Crystallographic Summary for 1,3-Diazaphenoxathiin

	A. Crystal Data (−110°C) [a]
a, Å	5.754(4)
b, Å	20.850(12)
c, Å	14.207(8)
V, Å^3	1704.5(17)
d_{measd} g cm^{-3} (25°C)[a]	1.526
d_{calcd} g cm^{-3} (−110°C)	1.576
Empirical formula	$C_{10}H_6N_2OS$
fw	202.23
Crystal system	orthorhombic
Space group	Pbca
Z	8
F(000), electrons	832
	B. Data Collection (−110°C) [b]
Radiation, λ (Å)	MoKα, 0.71069
Mode	omega scan
Scan range	symmetrically over 1.0° about Kα$_{1,2}$ maximum
Background	offset 1.0 and −1.0° in omega from Kα$_{1,2}$ maximum
Scan rate, deg min^{-1}	2.0 - 6.0
Exposure time, h	51.1
Stability analysis	
Computed a	−.000201
b	0.000006
Max. correction (on I)	0.5%
2θ range, deg	4.0 - 60.0
Range in hkℓ, min	0, 0, 0
max	8, 29, 19
Total reflections measd	2874
Data crystal dimensions, mm	0.31 × 0.30 × 0.12
Data crystal volume, mm^3	0.0113
Data crystal faces	102, 100, 010, 010, 021, 021 + fragmentary faces
Absorption coeff, μ(MoKα), cm^{-1}	3.35
Transmission factor range	0.919 - 0.964
	C. Structure Refinement [c]
Ignorance factor p	0.04
Reflections used, F ⩾ 5 °F	1492
No. of variables	151
Goodness of fit, S	1.26
R_1, R_2	0.0427, 0.0450
R_1 for all data	0.0890
Max shift/esd	0.010
Max peak in diff map (e Å^{-3})	0.36 (0.76 Å from C9A on S10-C9a vector)
Min density in diff map (e Å^{-3})	−.34

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with $20.7° < 2\theta < 28.1°$. Crystal density was measured by flotation in $ZnCl_2$ (aq). [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described by Riley and Davis [27]. Crystal and instrument stability were monitored by re-measurement of 4 check reflections after every 96 reflections. These data were analyzed as detailed by Henslee and Davis [28]. [c] Relevant expressions are as follows, where in this footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes.

Function minimized was $\Sigma w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$

$R_1 = \Sigma abs(F_o - F_c)/\Sigma F_o$

$R_2 = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$

From the x-ray crystallographic study of **6** which is discussed below, the molecular dihedral angle was determined to be $\phi = 165.5(9)°$ which is in excellent agreement with that predicted on the basis of the carbon nmr spectral data.

While considering the correlation of the chemical shift of the C-10a resonance of **6**, it is also worth noting what would be expected for the dihedral angle of the as yet unknown 2,4-diazaphenoxathiin (**9**) ring system. Assuming the calculated ^{13}C-nmr chemical shift of the C-10a angles expected for the molecule from linear regression analysis would be in the range of 132.2-134.9° which, on the average, represents a folding of 14.5° greater than that of the parent phenoxathiin ring system [18] ($\phi = 147.76°$). This expectation, if supported by experiment, would make the 2,4-diazaphenoxathiin (**9**) ring system the most extremely folded member of the phenoxathiin series yet to be described. Work on the synthesis of this ring system and others with highly electron withdrawn sulfur bearing quaternary carbons are at present underway in these laboratories and will be the subject of a future report.

X-Ray Crystallography.

Physical data for the crystal, data collection parameters and information about the structure refinement are contained in Table III. Final positional and thermal parameters are given in Table IV. The atomic labeling scheme is shown in Figure 2. Bond lengths and angles are shown in Figures 2 and 3 respectively, the observed data consistent with those of similar structures [5,23-26]. Least squares planes and deviations of atoms from the calculated planes are listed in Table V.

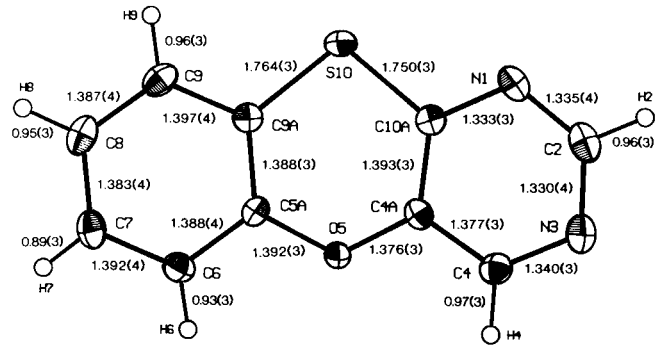


Figure 3. Bond angles for the non-hydrogen atoms of 1,3-diazaphenoxathiin (**6**).

Table IV

Atomic Positions in Fractional Coordinates and U (hydrogens) or U_{eq}[a] in 1,3-Diazaphenoxathiin

Atom	X	Y	Z	U
S10	.73813(11)	.43053(3)	.33500(4)	.0205(2)
C10A	.5632(4)	.49786(12)	.3546(2)	.0165(6)
N1	.6465(4)	.55345(10)	.32284(15)	.0228(6)
C2	.5159(5)	.60518(13)	.3392(2)	.0254(8)
N3	.3108(4)	.60749(10)	.3822(2)	.0238(6)
C4	.2287(5)	.55102(11)	.4125(2)	.0201(7)
C4A	.3517(4)	.49480(11)	.4021(2)	.0163(6)
O5	.2635(3)	.44044(7)	.44391(11)	.0191(5)
C5A	.3352(4)	.38005(11)	.4138(2)	.0162(6)
C6	.1900(4)	.32971(12)	.4388(2)	.0198(7)
C7	.2501(5)	.26727(11)	.4142(2)	.0230(7)
C8	.4529(5)	.25562(13)	.3647(2)	.0237(8)
C9	.5966(5)	.30626(12)	.3399(2)	.0217(7)
C9A	.5405(4)	.36918(12)	.3650(2)	.0172(7)
H2	.576(5)	.6457(14)	.320(2)	.035(9)
H4	.080(5)	.5510(11)	.444(2)	.017(7)
H6	.054(5)	.3397(12)	.471(2)	.021(7)
H7	.157(5)	.2358(13)	.435(2)	.027(8)
H8	.495(4)	.2134(13)	.347(2)	.018(7)
H9	.736(5)	.2964(13)	.306(2)	.033(8)

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

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* A_{ij}$$

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

Table V

Least Squares Planes in 1,3-Diazaphenoxathiin

Plane 1: S10, C10A, N1, C2, N3, C4, C4A, O5

$$-2.7463X - 3.4527Y - 12.2607Z + 7.6327 = 0$$

Deviations:

S10	0.0118(6)	C10A	0.019(2)	N1	−0.012(2)
C2	0.033(3)	N3	−0.004(2)	C4	0.044(2)
C4A	0.028(2)	O5	−0.054(2)		

Plane 2: S10, O5, C5A, C6, C7, C8, C9, C9A

$$-2.8078X + 2.3997Y - 12.2925Z + 5.1348 = 0$$

Deviations:

S10	−0.0225(6)	O5	−0.005(2)	C5A	0.019(2)
C6	−0.001(3)	C7	−0.017(3)	C8	0.007(3)
C9	0.017(3)	C9A	0.017(2)		

Dihedral angle: 163.85(5)°

Plane 3: C10A, N1, C2, N3, C4, C4A

$$-2.6642X - 3.0647Y - 12.4180Z + 7.4338 = 0$$

Deviations:

C10A	0.004(2)	N1	0.006(2)	C2	−0.008(3)
N3	−0.002(2)	C4	0.013(2)	C4A	−0.013(2)
S10	−0.0122(6)	O5	−0.131(2)		

Plane 4: C5A, C6, C7, C8, C9, C9A

$$-2.8475X + 2.1646Y - 12.2570Z + 5.2068 = 0$$

Deviations

C5A	0.003(2)	C6	0.002(3)	C7	−0.003(3)
C8	0.000(3)	C9	0.005(3)	C9A	−0.007(2)
S10	−0.0691(6)	O5	−0.031(2)		

Dihedral angle: 165.46(8)°

Molecular packing is illustrated in Figure 4, molecules packing along the *a* axis as centrosymmetric pairs interacting through S10—O5 (1 + x, y, z; 3.403(2) Å) and O5—H4 (x, 1-y, 1-z; 2.54(3) Å) contacts. Along the *b* axis, the closest contact is N3—H7 (½-x, ½ + y, z) at 2.78(3) Å.

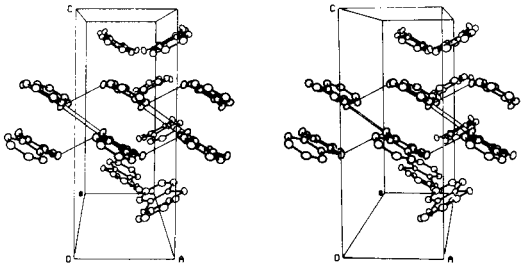


Figure 4. Crystal packing diagram for 1,3-diazaphenoxathiin (**6**). Lines connecting individual molecules illustrate close contacts through S10---O5 and O5---H4 along the *a* axis and through N3---H7 along the *b* axis.

EXPERIMENTAL

All solvents used were reagent grade or better and, with the exception of the *N,N*-dimethylformamide which was distilled from calcium hydride, were freshly distilled and stored over 3 Å Linde molecular sieves. Melting points were obtained in open capillary tubes on a Thomas-Hoover melting point apparatus and are reported uncorrected. Infra-red spectra were recorded on a Perkin-Elmer model 283 spectrophotometer as potassium bromide pellets. The ^{13}C-nmr spectra were recorded in deuteriochloroform on a Varian XL-100-15 spectrometer equipped with a Nicolet NIC-1180 computer interfaced through a model 239A' pulse programmer. Conventionally broad band decoupled spectra were obtained with a decoupling field of $\gamma H_2/2\pi$ = 2.9 KHz centered on the solvent frequency. The following instrument parameters were used: pulse width = 12 μsec (90° pulse = 19 μsec); interpulse delay = 8 sec; spectral width = ±2500 Hz digitized with 8K data points for decoupled and 16K data points for coupled spectra affording acquisition times of 0.8192 and 1.6384 sec respectively. Chemical shifts were referenced relative to the central line of the residual chloroform multiplet which was taken as 77.0 ppm downfield of tetramethylsilane.

1,3-Diazaphenoxathiin (**6**).

To a suspension of 0.069 g (0.003 mole) of sodium hydride in 40 ml of dry, distilled DMF was added 0.183 g (0.0015 mole) of *o*-mercaptophenol under an inert argon atmosphere. The suspension was stirred at room temperature overnight and was then cooled (ice bath), after which 0.28 g (0.0015 mole) of 5-bromo-4-chloropyrimidine (**3**), prepared according to the procedure of Chesterfield, McOmie and Sayer [15], in 40 ml of DMF was added. The reaction mixture was allowed to warm to room temperature and was then refluxed for five hours. Upon cooling, the reaction mixture was poured into 200 ml of ice cold distilled water, the resultant mixture extracted with 3 × 150 ml portions of ethyl acetate. The combined ethyl acetate extracts were then washed with 2 × 100 ml of 5% aqueous sodium bicarbonate followed by 2 × 100 ml of distilled water, after which the ethyl acetate solution was dried over anhydrous sodium sulfate and concentrated. The crude product was chromatographed over silica gel using a linear gradient elution with a solvent system which was varied from pure heptane to a mixture of heptane:ethyl acetate (6:5) to afford 0.040 g (14% yield) of a white crystalline solid which melted 101-103°. The infrared spectrum showed λ (cm^{-1}): 3040, 1590, 1550, 1470, 1440, 1425, 1390, 1290, 900, 820, 760 and 730. The electron impact mass spectrum gave: m/z (% relative intensity) M^+ = 202 (100); $M^+ + 1$ = 203 (13); $M^+ + 2$ = 204 (6); $M^+ - HCN$ = 175 (11); $M^+ - S$ = 170 (2); $M^+ - CS$ = 158 (5). The ^{13}C-nmr calculated and assigned chemical shifts are contained in Table I. Heteronuclear spin-coupling constants are collected in Table II.

Anal. Calcd. for $C_{10}H_6N_2OS$: C, 59.39; H, 2.99; N, 13.85. Found: C, 59.32; H, 3.04; N, 13.85.

X-Ray Crystal Structure Determination.

A summary of the crystal data, data collection parameters and structure refinement is given in Table III. The $\sigma(I)$ and σF_o) were determined in the manner described by Stout and Jensen [19] where p = 0.04. All non-hydrogen atoms were located in the E-map phased by the best solution from MULTAN78 [20]. Hydrogen atoms were located in a difference map at electron densities of 0.51 - 0.75 e/Å^3 at a stage where R = 0.056. All atomic positions, non-hydrogen anisotropic thermal parameters and hydrogen isotropic thermal parameters were refined by full-matrix least squares using SHELX76 [21]. Scatterning factors and anamolous dispersion corrections were used as contained in SHELX76. Other programs used are listed by Gadol and Davis [22].

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