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SYNTHESIS AND SPECTROSCOPY OF 1,2,5-SELENADIAZOLO-[3.4-b]-PYRIDINE AND 1,2,5-SELENADIAZOLO-[3.4-c]-PYRIDINE

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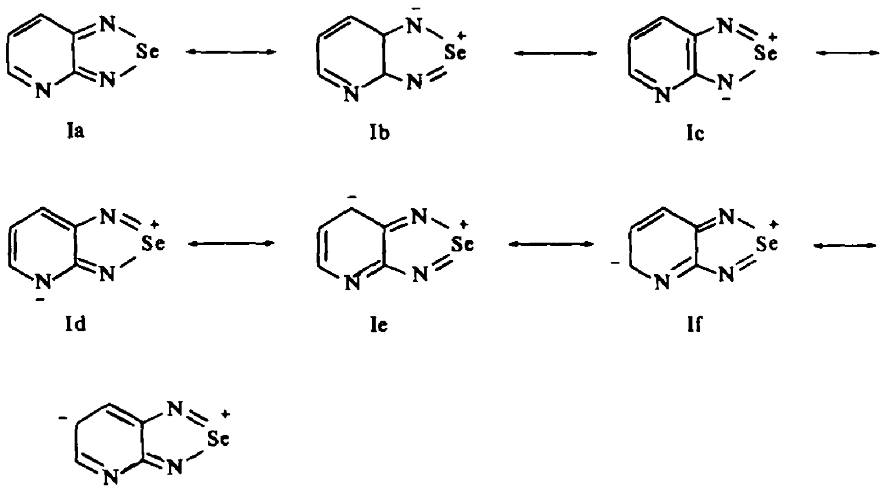
Abstract—The novel 1,2,5-selenadiazolo[3.4-b]pyridine and 1,2,5-selenadiazolo[3.4-c]pyridine have been synthesized. Their IR, UV and PMR spectra are reported and discussed.

INTRODUCTION

1,2,5-SELENADIAZOLO[3.4-b]PYRIDINE (I) and 1,2,5-selenadiazolo[3.4-c]pyridine (II) are the two possible pyrido-analogues of the known benzo-2,1,3-selenadiazole[1,2] and 1,2,5-selenadiazolo[3.4-d]pyrimidine[3] ring systems. They, in common with the latter two compounds, are potentially ten π-electron systems the structure of which can be considered in terms of the various canonical forms shown (Ia–g and IIa–g, etc). While a tentative identification of the related 1,2,5-oxadiazolo[3.4-b]pyridine[4] has been reported, the two selenadiazolopyridines (I and II) described appear to be novel compounds. By analogy to the ready synthesis of benzo-2,1,3-selenadiazole they have been made, in relatively low yields, by the reaction of 2,3-diamino- and 3,4-diaminopyridine with selenium dioxide. Herein we report their preparation, IR, UV and PMR spectra.



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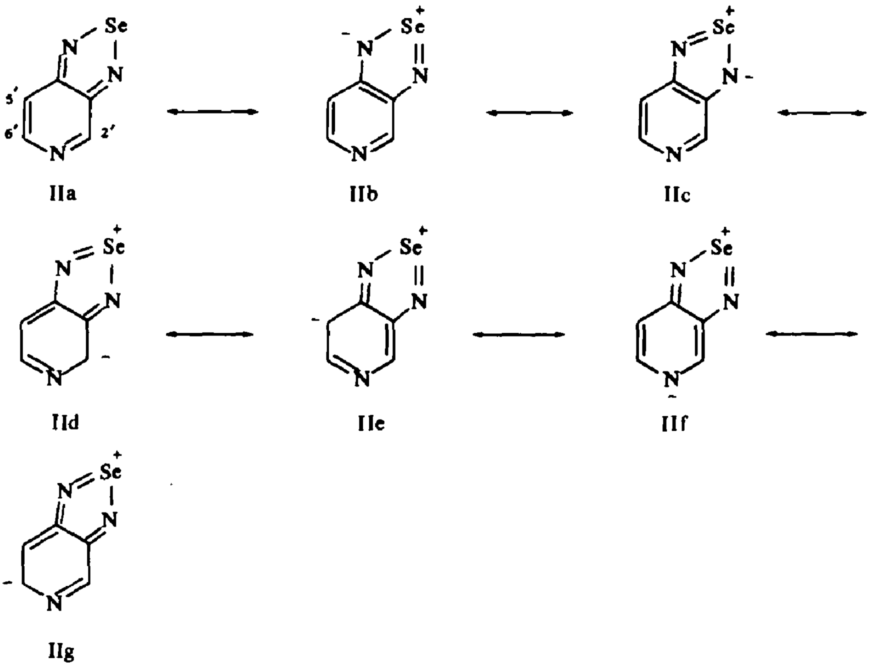

TABLE 1[a]. IR ABSORPTION BANDS (cm^{-1}) OF 1,2,5-SELENADIAZOLO[3,4-B]PYRIDINE (I) AND 1,2,5-SELENADIAZOLO[3,4-C]PYRIDINE (II)

I	II	Assignment[b]
1588 m	1580 m	
1500 s	1482 w	$\nu_{C—C}$ and $\nu_{C—N}$ modes
1482 m	1450 w	
	1430 m	
1372 w	1358 w	ring modes of both 5- and 6-membered rings
	1340 w	
1286 w	1272 m	diazole ring modes
	1268 m	
1208 m	1228 w	
1128 m	1168 w	β-CH and ring modes
998 m	1002 m	
916 w		
814 m	905 s	
808 m	824 s	γ-CH found in 2,3- and 3,4-disubstituted pyridine
	810 m	
780 s		
750 m	752 m	γ-CH
720 m	710 m	ring modes of both rings
	625 s	
594 m	570 s	diazole ring modes
550 w	562 s	
498 m	492 m	diazole ring modes

[a] KBr discs were used.

[b] ν: stretching mode; β and γ, in- and out-of-plane deformations, respectively.

IR and UV spectra

The bands of significant intensity in the IR spectra of 1,2,5-selenadiazolo[3.4-b] and [3.4-c]pyridine are given in Table 1. By analogy with known bands in pyridine, 2,3-disubstituted and 3,4-disubstituted pyridines[5] and in 1,2,5-selenadiazole[6] some of the bands have been tentatively assigned as indicated.

The corresponding details of their UV spectra are given in Table 2. In both cases the absorption spectrum showed only one broad symmetrical intense band with, as expected, no vibrational fine structure apparent. The position and intensity of the observed band in both compounds correspond closely to those of the $\pi \rightarrow \pi^*$ band in benzo-2,1,3-selenadiazole.[7] Unlike the latter,[8] however, in neither of the selenadiazolopyridines can an $n \rightarrow \pi^*$ band be identified separately from the main absorption.

TABLE 2. UV ABSORPTION BANDS OF 1,2,5-SELENADIAZOLO[3.4-B]PYRIDINE (I) AND 1,2,5-SELENADIAZOLO[3.4-C]PYRIDINE (II)

Compounds	Solvent	λ_{max} (mμ)	$\text{Log}_{10}\ \varepsilon$
I	$CHCl_3$	336	4·215
	EtOH	332	4·137
II	$CHCl_3$	320	4·013
	EtOH	320	3·987

PMR spectra

The PMR spectra of 1,2,5-selenadiazolo[3.4-b] and [3.4-c]pyridine were of near first order AMX type. The spectrum of the former showed all the twelve lines expected while in that of the latter only eight were observed implying that in it, one of the three coupling constants was close to zero. The two observed spectra are shown in Figs 1 and 2 respectively, along with the corresponding spectra calculated from

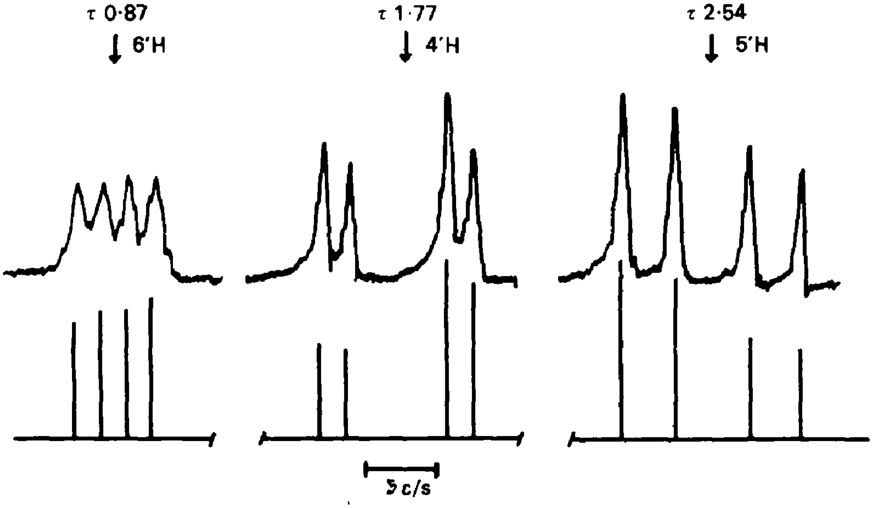

FIG. 1

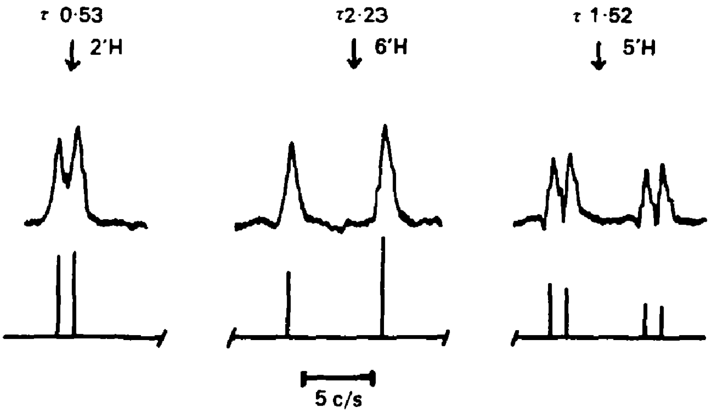

FIG. 2

the refined chemical shifts and coupling constants given in Table 3. The programmes used for iterative refinement of the observed parameters (with line positions averaged from a number of spectra swept in both field directions) and for the calculation of the spectra given are based[9] on NMREN and NMRIT of Swalen and Reilly.[10] For these calculations it was assumed that all the coupling constants were positive. The

TABLE 3 . PMR PARAMETERS OF 1,2,5-SELENADIAZOLO[3.4-B]PYRIDINE (I) AND 1,2,5-SELENADIAZOLO[3.4-C]PYRIDINE (II)

Compound	Chemical shifts (τ)			Coupling constants (J c/s)		
I	4'H	5'H	6'H	4'H–5'H	4'H–6'H	5'H–6'H
	1·76$_5$	2·54$_7$	0·87$_1$	9·10$_9$	1·82$_2$	3·64$_9$
II	2'H	5'H	6'H	2'H–5'H	2'H–6'H	5'H–6'H
	0·52$_6$	2·22$_7$	1·51$_5$	1·18$_9$	0·01$_7$	6·66$_4$

[a] CDCl$_3$ solutions were used.

chemical shift and coupling assignments given follow from a consideration of the magnitudes of the coupling constants and the known shifts in pyridines[11,12] and benzo-2,1,3-selenadiazole.[13]

In the spectrum of 1,2,5-selenadiazolo[3.4-b]pyridine (I) the low field quartet has a slightly greater observed line-width than the other lines present. This has been taken to show the presence of an adjacent N atom, the quadrupolar nature[14] of which is the cause of the broadening noted. Hence the assignment of this quartet to the C(6')-hydrogen by analogy to the situation in pyridine itself.[15] The larger of the two *ortho*-coupling constants found, is expected (on the basis of the suggested double bond character of the intervening bond, Ia–g) to be that between C(4') and C(5') hydrogen and since the smallest of the three couplings will be between non-adjacent

H atoms, the assignments given must follow. The two *ortho*-couplings and *meta*-coupling found are in reasonable agreement with the ranges reported for such coupling constants in substituted pyridines.[11, 12] Typically, these are 7·4–7·8 c/s and 3·9–5·1 c/s for the two distinct *ortho*-couplings generally observed, and 1·4–2·5 c/s for *meta*-couplings.

The largest coupling constant in the eight line spectrum of 1,2,5-selenadiazolo-[3.4-c]pyridine (II) must be between the C(5′) and C(6′) H atoms with the smallest across the nitrogen in the fused pyridine ring rather than that between the hydrogens at C(5′) and C(2′). In this way the chemical shifts, as assigned, appear to be more acceptable than the alternative in which the C(6′) hydrogen is at high field. The chosen assignment gives a *para*-coupling constant for the C(2′) and C(5′) hydrogens comparable with that in correspondingly substituted pyridines, generally 0·6–1·2 c/s.[11, 12] However, the *ortho*-coupling constant between the hydrogens at C(5′) and C(6′) is significantly larger than in other pyridines. This can be taken to imply a high degree of bond fixation in the intervening C—C bond.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 125 spectrophotometer using KBr discs and the UV spectra were obtained on a Perkin–Elmer 137 spectrophotometer using spectroscopic EtOH and $CHCl_3$ as solvents. The PMR spectra were run, without degassing on a Perkin–Elmer R10 spectrometer operating at 40·004 Mc/s, at 33·5°, on $\sim$10% w/v $CDCl_3$ solns internally referenced to TMS.

1,2,5-*Selenadiazolo*[3.4-b]*pyridine* (I). 2,3-Diaminopyridine (2·18 g) was refluxed with SeO_2 (2·2 g) in excess benzene under a Dean and Stark apparatus till no more water was distilled off. The resultant deep red soln. was filtered hot and then evaporated *in vacuo*, leaving a red residue which was taken up in 1:1 diethyl ether–acetone and then filtered through charcoal. The filtrate was reduced in bulk and by the addition of excess light petroleum (b.p. 40–60°) a yellow solid was precipitated. This was redissolved in 1:1 diethyl ether–acetone, filtered again through charcoal and reprecipitated with light petroleum to give I as a canary yellow solid (1·3 g, 36%), m.p. 116–118°. (Found; C, 33·2; H, 1·9; N, 22·5. $C_5H_3N_3Se$ requires: C, 32·3; 1·6; N, 22·7%).

1,2,5-*Selenadiazolo*[3.4-c]*pyridine* (II). 3,4-Diaminopyridine (0·54 g) was refluxed as above with SeO_2 (0·55 g). Similar treatment gave a dark red residue which was taken up in diethyl ether and filtered through charcoal. The addition of excess light petroleum (b.p. 40–60°) to the filtrate gave a ppt. (II) as a dark red solid (0·1 g, 11%), m.p. 181°. (Found; C, 32·8; H, 1·9; N, 21·8. $C_5H_3N_3Se$ requires: C, 32·3; H, 1·6; N, 22·7%).

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