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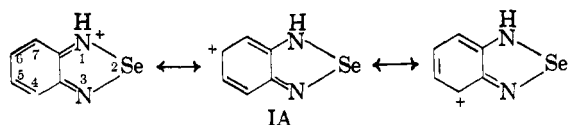
Structure of 2,1,3-Benzoselenadiazole and Its Derivatives.**II. Position of the Proton¹**EUGENE SAWICKI² AND ALBERT CARR³

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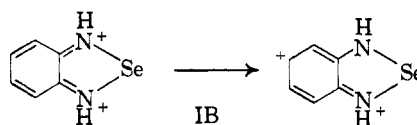
From an investigation of the ultraviolet-visible absorption spectra of 4- and 5-substituted derivatives of 2,1,3-benzoselenadiazole in acid solution the position of proton addition was determined. Strong spectral differences were shown to exist between 4- and 5-substituted derivatives and between the bases, monocationic salts, and the dicationic salts.

In a previous paper⁴ the preparation and absorption spectra in alcohol of 2,1,3-benzoselenadiazole, I, and its derivatives have been discussed. The five-membered heterocyclic ring in 2,1,3-benzoselenadiazole has been shown to be strongly electron-attracting. It was decided to investigate the spectral properties of this ring system in acid solution. Knowledge of these properties would be of great value in proof-of-structure and analytical work involving this and analogous ring systems.

The absorption spectrum of I in strong sulfuric acid solutions indicates that this molecule can add 2 protons. There is a high electron density on the ring nitrogens of I for, as shown in the previous paper,⁴ structures containing a negative charge on the ring nitrogen and a positive charge in the benzene ring contribute strongly to the excited state. Consequently the first proton adds to a ring nitrogen. In fact a perchlorate of I can be isolated as canary-yellow crystals.⁵ Because the structures contributing strongly to the excited state of the monocationic salt, IA, do not involve a separation of charge as is involved in the excited state of the base, the spectrum of the salt shows a red shift, Table I.



Structures involving a positive charge on the selenium or on the 3-nitrogen could also be expected to have some contribution to the excited state. These latter interfering structures would have little or no contribution to the excited state of the dicationic



salt, IB. Consequently the dicationic salt shows a red shift in its spectrum, Table I.

A methyl group attached to the positive resonance terminal of a conjugated system causes a red shift in the absorption spectrum.^{6,7} This effect is shown in the spectrum of 5-methyl-2,1,3-benzoselenadiazole in alcohol and acid solutions, Table I. In the 5-methoxy compound and its salts there is a positive charge on the methoxy group in the excited state. This structure is of much lower energy than comparable excited state structures of I involving a positive charge on a carbon atom of the benzene ring. Consequently the 5-methoxy compound and its salts show a definite red shift in their long wave-length band as compared to I and its salts, Table I.

Derivatives of I substituted in the 5-position show an increasing shift toward the visible of their long wave-length band with the following substituents $H < CH_3 < OCH_3 < C_6H_5 < SCH_3 < NH_2 < NMe_2$, Table I. This order refers to the bases, the monocationic salts and, except for the more strongly basic amino compounds, the dicationic salts. The same order has been found in *para*-substituted triphenylmethane dyes.⁷ In all cases, except for the more basic amino compounds, the dicationic salt absorbed at longest wave length while the base absorbed at the shortest wave length. This effect is shown in the spectra of 5-methylthio-2,1,3-benzoselenadiazole and its salts, Fig. 1. The same explanation can be given for this phenomenon as was given for I and its salts.

The behavior of the amino compounds is exceptional. In the 5-amino and 5-dimethylamino compounds the first proton probably adds to the 3-nitrogen.

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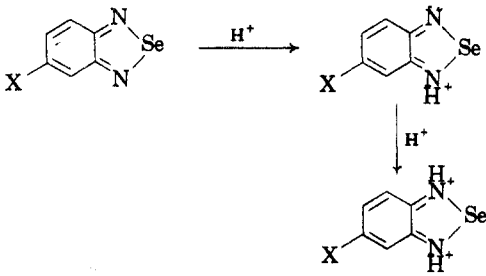
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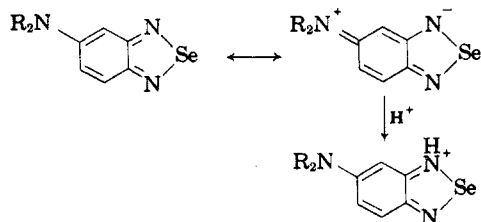
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TABLE I
ABSORPTION SPECTRA OF 5-SUBSTITUTED PIASELENOLES



X	λ_{\max} (Log ϵ)		
	95% EtOH	50% H ₂ SO ₄ ^a	95% H ₂ SO ₄ ^b
H	231 (3.66) 331 (4.22)	222 (3.83) 250 ^c (3.25) 341 (4.26) 380 (3.29)	222 (4.00) 260 (3.05) 350 (4.28) 362 (4.36) 435 (2.93)
CH ₃		226 (3.94) 250 (3.28) 347 (4.32) 390 (3.35)	
OCH ₃	240 (3.65) 329 (4.04) 358 (3.88)	234 (3.85) 355 (4.15) 386 (3.92)	234 (4.13) 288 (3.16) 365 (4.23) 475 (3.69) 257 (4.24) 340 (3.95) 402 (4.01) 550 (3.92)
C ₆ H ₅	238 (4.08) 253 (4.34) 346 (4.24) 370 (3.94)		
SCH ₃	246 (4.19) 340 (3.94) 390 (3.99)	254 (4.09) 292 (3.44) 364 (3.93) 448 (4.14)	268 (4.24) 290 (3.44) 336 (3.75) 394 (3.94) 572 (4.08)
NH ₂	236 (4.25) 266 (3.64) 324 (3.94) 425 (3.80)	236 (3.97) 333 (4.10) 459 (3.74)	222 (3.82) 242 (3.48) 337 (4.25) 380 (3.35)
N(CH ₃) ₂	242 (4.26) 247 (4.25) 280 (3.62) 326 (3.88) 449 (3.83)	224 (4.10) 246 (3.99) 310 (3.8) 334 (3.89) 503 (3.77)	218 (3.75) 244 (3.48) 337 (4.21) 380 (3.28)

^a The spectral data for the amino compounds were determined in 50% alcoholic 1.2*N* hydrochloric acid. ^b The spectral data for the amino compounds were the same in 50% sulfuric acid as in 95% sulfuric acid. In this case the second proton has added to the amino nitrogen. ^c Underlined values are shoulders.



If it added to the amino nitrogen, the resultant salt would have a spectrum closely similar to that

of I. Instead there is a red shift, Table I. As the 3-nitrogen has a greater electron density than the 1-nitrogen, the proton must add to the 3-nitrogen. In all the compounds studied this position is probably where the first proton adds, although the possibility of the additional presence of tautomeric salts, involving proton addition to the 1-nitrogen or to the 5-amino nitrogen, cannot be excluded. In this respect the presence of tautomeric 4-aminoazobenzene cationic salts has been shown.^{8,9} Addition of the second proton must take place at the amino nitrogen, for the spectrum of this dicationic salt is closely similar to the iso-*pi*-electronic monocationic salt of I, Table I.

In 4-amino-2,1,3-benzoselenadiazole the first proton must add to the amino group to give a monocationic salt iso-*pi*-electronic with I, for the spectrum of this salt is closely similar to the spectrum of I. In the 4-aminoazobenzene monocationic salts it has been shown that with increasing acidity the longer wave length absorbing cationic resonating tautomer increases at the expense of the ammonium zwitterionic-resonating tautomer.⁹ In the same way in a solution of optimum acidic strength the tautomer involving proton addition to the 1-nitrogen of a 4-amino derivative of I might be capable of existence.

The second proton must add to the 1-nitrogen for the spectrum of this dicationic salt is closely similar to the spectra of the dicationic salts of the 5-amino-I derivatives and the monocationic salt of I, Tables I and II (see Fig. 2 also). These spectra resemble

TABLE II
ABSORPTION SPECTRA OF MISCELLANEOUS DERIVATIVES OF 2,1,3-BENZOSELENADIAZOLE

Substituent	λ_{\max} (log ϵ)	
	95% EtOH	95% H ₂ SO ₄
4-C ₆ H ₅	251 (4.12) 332 (4.20) 340 (4.25) 373 (3.62)	240 (4.19) 350 (4.23) 442 (3.2) ~560 ^a (2.8)
4-NH ₂ ^{b,c}	242 (4.14) 330 (4.04) 462 (3.28)	221 (3.82) 250 (3.21) 340 (4.28) 380 (3.29)
5-SO ₂ CH ₃	244 (3.84) 334 (4.27) 358 (3.58)	240 (3.80) 342 (4.29) 380 (3.32)
5-NO ₂ ^e	230 (3.71) 274 (4.02) 342 (4.21)	224 (3.86) 274 (4.03) 348 (4.22) 385 (3.4)

^a All underlined values are shoulders. ^b 4-Amino-I has λ_{\max} (log ϵ) values in 50% alcoholic 1.2*N* HCl of 231 (3.70); 332-334 (4.23). ^c The absorption spectrum of this compound in 50% H₂SO₄ is almost identical to that in 95% H₂SO₄.

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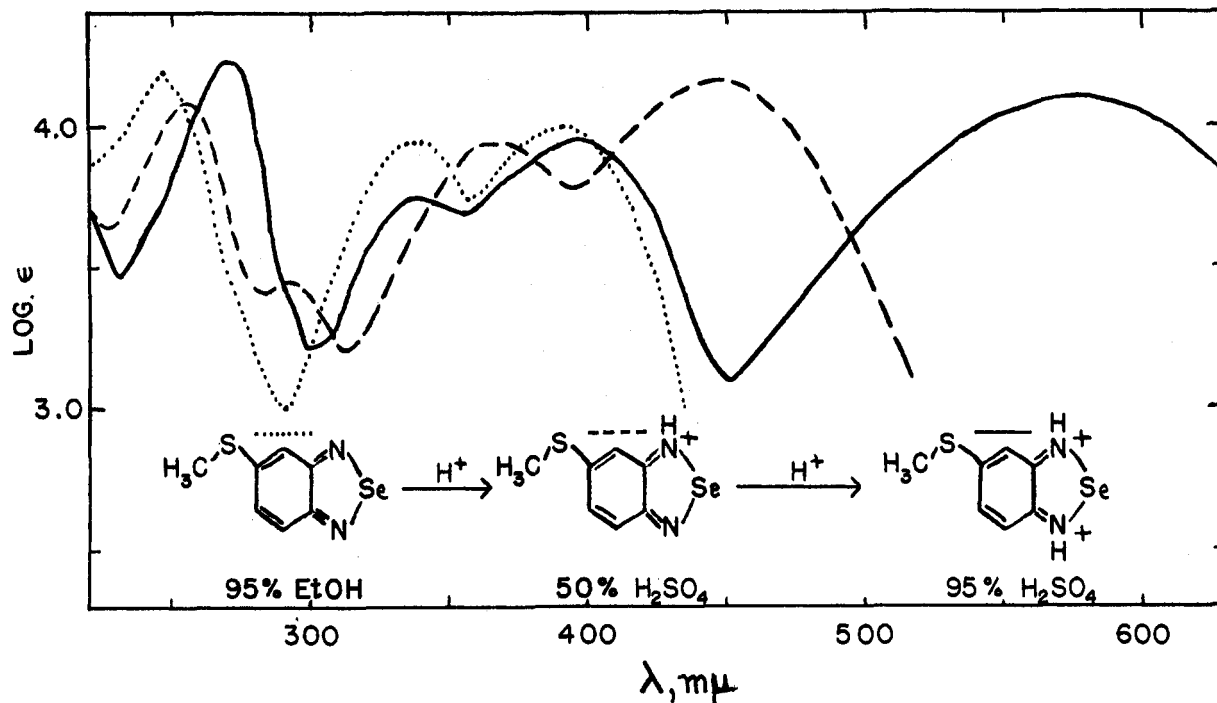


FIG. 1. ULTRAVIOLET-VISIBLE ABSORPTION SPECTRUM OF 5-METHYLTHIO-2,1,3-BENZOSELENADIAZOLE in 95% ethanol; in 50% alcoholic sulfuric acid ----; in 95% sulfuric acid ———.

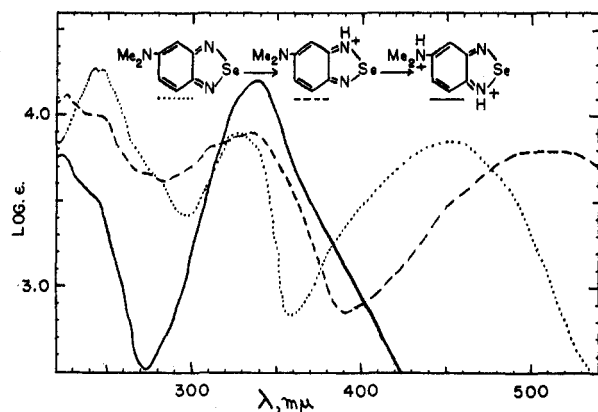


FIG. 2. ULTRAVIOLET-VISIBLE ABSORPTION SPECTRUM OF 5-DIMETHYLAMINO-2,1,3-BENZOSELENADIAZOLE in 95% ethanol; in 50% alcoholic 6*N* hydrochloric acid ----; in 95% sulfuric acid ———.

the spectra of the 5-nitro and 5-methylsulfonyl derivatives of I in 95% sulfuric acid. In these electro-negatively substituted I derivatives it appears that only one proton adds in the solvent system em-

ployed. The spectrum of the 5-nitro derivative in alcohol and in 95% sulfuric acid shows a band at 274 $m\mu$ which must be derived from interaction of the nitro group with the remainder of the molecule. In this respect nitrobenzene has been shown to have its main band at 260 $m\mu$ in alcohol.¹⁰

EXPERIMENTAL⁷

Preparation of compounds. The compounds studied in this paper were prepared by the procedures cited in a previous paper.⁴

Ultraviolet-visible absorption spectra. The absorption spectra were determined with a Beckman Model DU Quartz Spectrophotometer. Essentially "50%" sulfuric acid consists of 50 ml. concentrated sulfuric acid diluted to 100 ml. with 95% ethanol; "95%" sulfuric acid consists of 5 ml. 95% ethanol diluted to 100 ml. with concentrated sulfuric acid.

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