BENZO-2,1,3-THIASELENAZOLIUM SALTS

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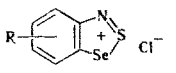
We have found that the reaction of thionyl chloride with o-aminoselenophenol hydrochlorides gives benzo-2,1,3-thiaselenazolium salts (I) in 75-83% yields. These new heterocyclic cations, which are 1-selenium analogs of Herz salts, are precipitated from solution by the addition of absolute ether. The salts were purified by fractional precipitation.

Signals of aromatic protons corresponding to three-spin systems of the ABC type (Ib, c) and four-spin systems of the ABCD type (Ia) were observed in the PMR spectra of these compounds.



I a,b,c

a R = H; b R = 6-Cl, c R = 5-Cl

The spectra of trifluoroacetic acid solutions of the compounds were recorded with a Varian HA-100 spectrometer with an operating frequency of 100 MHz. Cyclohexane was used as the reference signal for internal stabilization of the resonance conditions and as the internal standard. The chemical shifts (δ) and spin–spin coupling constants (J) are presented in Table 1.

As compared with the isomeric benzo-1,2,3-thiaselenazolium salt, the signals of the protons of Ia are shifted to weak field by 0.2 ppm. The average difference in the chemical shifts of the α and β protons for Ia is 0.2 ppm greater than for benzo-1,2,3-thiaselenazolium and benzo-1,2,3-dithiazolium salts and amounts to 0.7 ppm; this constitutes evidence for the high magnetic anisotropy of the heteroring. Compounds Ia, b, c have higher colors than the corresponding benzo-1,2,3-thiaselenazolium salts.

TABLE 1. Benzo-2,1,3-thiaselenazolium Chlorides

Structure	Empirical formula	Found, %		Calc., %		UV spectrum		PMR spectrum: chemical shifts, δ ppm,				PMR spectrum: spin–spin coupling constants, J, Hz			
		Cl	N	Cl	N	λ_{max}, nm	lg ε	4-H	5-H	6-H	7-H	$J_{4,5}$	$J_{6,7}$	$J_{4,6}$	$J_{5,7}$
Ia	$C_6H_4ClNSSe$	15,4	6,1	15,0	5,9	455 361	3,28 3,98	9,19	8,24	8,46	9,04	8	9		
Ib	$C_6H_3Cl_2NSSe$	26,3	5,0	26,2	5,2	450 380	3,45 3,86	9,02	8,13	—	8,98	7,4	—	—	2
Ic	$C_6H_3Cl_2NSSe$	26,5	5,1	26,2	5,2	460 370	3,20 3,98	9,17	—	8,34	8,98	—	10	2	—

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