BENZO-1,2,3-DISELENAZOLIUM SALTS

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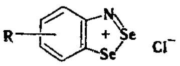
UDC 547.794

Previously unknown benzo-1,2,3-diselenazolium salts (Ia-c) were synthesized in 79-90% yields by reaction of selenious acid with o-aminoselenophenol hydrochlorides in acetic and formic acids.



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

Chlorides Ia-c were purified by fractional precipitation by means of absolute ether from solutions in formic acid and by crystallization from formic acid and acetic anhydride, after which satisfactory results were obtained in the analysis for Cl and N. The following chemical shifts and spin–spin coupling constants were found in the PMR spectrum of Ia at 100 MHz: δ_4 771.4, δ_5 662.6, δ_6 707.8, and δ_7 738.5 Hz (relative to cyclohexane as the internal standard with CF_3COOH as the solvent); $J_{4,7} = 9.2$, $J_{5,6} = 6.9$, $J_{6,7} = 8.6$, $J_{6,7} = 8.6$, $J_{4,6} = 1.2$, and $J_{4,7} < 0.2$ Hz. A comparison of these values with those calculated within a first-order approximation showed that the error in the determination of the spectral parameters did not exceed 2 Hz. The relationship $J_{ortho} \gg J_{meta} > J_{para}$ is also satisfied in the case of Ib, c, and this, in conjunction with the large range of the shielding constants of the aromatic protons, ensures a confident interpretation of the spectra in accordance with the first-order rules. One's attention is directed to the large difference in the chemical shifts of the aromatic protons in Ia-c, which is probably associated with the local contributions of the π electrons to the shielding constant and with the effect of the anisotropy of the heteroring. Salts Ia-c are more deeply colored than the corresponding Hertz salts and their monoselenium analogs. The electronic spectra are characterized by the following λ_{max} values, nm (log ε) (in 93% H_2SO_4): 470 (3.54) and 400 (4.02) for Ia, 450 (3.21) and 392 (4.04) for Ib, and 470 (3.57) and 398 (4.08) for Ic.

Leningrad Branch, All-Union Scientific-Research Institute of Synthetic Fibers. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1429-1430, October, 1975. Original article submitted February 10, 1975.