CHEMISTRY OF BENZO[b]SELENOPHENE

II.* PMR SPECTRA OF THE DEUTERO DERIVATIVES OF A NUMBER OF BENZO[b]SELENOPHENES

N. N. Magdesieva, V. A. Vdovin,
and N. M. Sergeev

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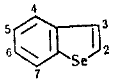
2-Deutero-, 3-deutero-, 2,3-dideutero-, 2-methyl-3-deutero-, and 3-methyl-2-deutero-benzo[b]selenophenes were synthesized, and their PMR spectra were interpreted.

In this paper we have studied the PMR spectra of benzo[b]selenophene and methylbenzo[b]selenophene and their deutero derivatives in order to use the results for the study of the direction of electrophilic substitution in the condensed aromatic system of benzo[b]selenophene.

From the point of view of the magnetic equivalence of the protons, the benzo[b]selenophene molecule can be considered to be a six-spin ABCD MN system,



the overall spectrum of which will consist of the spectra of independent ABCD groups (benzene ring protons) and MN groups (selenophene ring protons).† As seen from Fig. 1, the signals of the protons of the selenophene ring are superimposed on the multiplet signals of the benzene protons in the PMR spectrum of benzo[b]selenophene; this therefore makes it impossible to assign the signals of the α and β protons of the selenophene ring on the basis of only the spectrum of benzo[b]selenophene.

We therefore synthesized various deutero derivatives of benzo[b]selenophene and methylbenzo[b]selenophenes and investigated their PMR spectra.

The resonance signals of unsubstituted α and β protons in 2- and 3-methylbenzo[b]selenophenes were assigned first. Thus we were able to isolate the signal of the proton of the selenophene ring in the PMR spectrum of 3-methylbenzo[b]selenophene by double nuclear resonance. Since this proton experiences a spin–spin coupling with the protons of the methyl group (J = 1.2 Hz), by irradiating the methyl protons we isolated a singlet signal of the proton in the 2 position of the 3-methylbenzoselenophene molecule with a chemical shift of 7.33 ppm from the overall multiplet at 7.0-7.8 ppm (Fig. 2). The signal of the proton in the 3 position with a chemical shift of 6.97 ppm was similarly isolated from the multiplet signal at 6.80-7.75 ppm in the PMR spectrum of 2-methylbenzo[b]selenophene. The constants of the interaction of the protons of the methyl groups with the adjacent protons of the selenophene

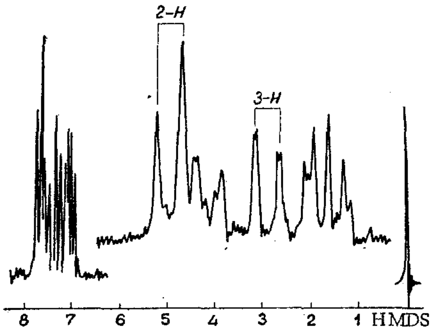


Fig. 1. PMR spectrum of benzo[b]selenophene (2% solution in CCl_4).

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*See [1] for communication I.

†We are not considering molecules that contain a magnetic Se^{78} isotope, in connection with their low percentage (7.5%) and the difficulty involved in analyzing the spectra that arise.

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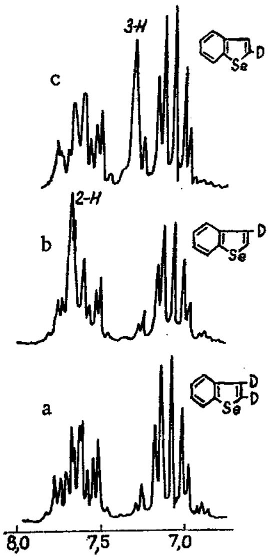

Fig. 2. PMR spectrum of 3-methylbenzo[b]selenophene (10% solution in CCl_4): a) single resonance spectrum; b) double resonance spectrum with irradiation of the methyl proton; c) doublet of the methyl proton.

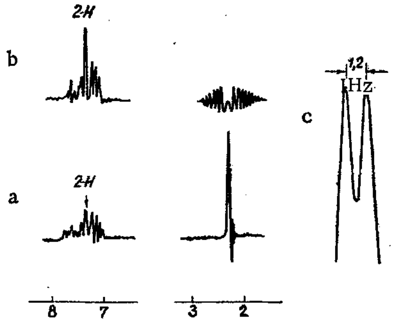

Fig. 3. PMR spectra (10% solutions in CCl_4): a) 2-deuterobenzo[b]selenophene; b) 3-deuterobenzo[b]selenophene; c) 2,3-dideuterobenzo[b]selenophene.

ring for the methyl derivatives of benzo[b]selenophene are comparable to the corresponding constants in derivatives of benzo[b]thiophene, benzo[b]furan, and indole (1.2-1.5 Hz) [2,3].

The assignment of the signals of the α and β protons of the selenophene ring in methylbenzo[b]selenophenes was confirmed by an investigation of the PMR spectra of the corresponding deutero derivatives of 2-methyl- and 3-methylbenzo[b]selenophene.

Instead of a doublet, the PMR spectrum of 2-methyl-3-deuterobenzo[b]selenophene has a singlet from the protons of the methyl group with a chemical shift of 2.57 ppm, and the signal of a proton in the 3 position with a chemical shift of 6.97 ppm is absent.

A doublet with a splitting of 11.3 ± 0.5 Hz is observed along with the major singlet of the methyl protons in the spectrum of 2-methyl-3-deuterobenzo[b]selenophene. Judging from the relative intensity of this doublet, this splitting is apparently caused by interaction of the protons of the methyl group with the Se^{77} isotope. This is also attested to by the fact that the doublet signal of the methyl protons in the PMR spectrum of 2-methylbenzo[b]selenophene also has two satellites with an interaction constant of 11.3 ± 0.5 Hz. The same sort of constant ($J_{Se^{77}-\beta=H} = 9.5$ Hz) was also observed in selenophene [4].

The PMR spectrum of 3-methyl-2-deuterobenzo[b]selenophene contains the expected singlet from the methyl protons with a chemical shift of 2.25 ppm, but the signal of a proton in the 2 position with a chemical shift of 7.33 ppm is absent (Fig. 2).

If the contribution of the methyl group to shielding of the adjacent proton of the benzo[b]thiophene derivatives [5,3] is assumed to be 0.39-0.40 ppm for 3-methylbenzo[b]thiophene and 0.39 ppm for 2-methylbenzo[b]thiophene, the signals of the protons in the 2 and 3 positions of unsubstituted benzo[b]selenophene should be found at ~7.73 ppm and ~7.35 ppm, respectively. In fact, the two most intense doublet signals in the expected region can be isolated from the multiplet at 6.87-7.87 ppm in the PMR spectrum of benzo[b]selenophene (Fig. 1). This is a doublet from the proton in the 2 position with a chemical shift of 7.71 ppm (J = 6.0 Hz) and a doublet signal from the proton in the 3 position with a chemical shift of 7.31 ppm (J = 6.0 Hz). Similar spin–spin coupling constants are observed for the corresponding protons in the benzo[b]thiophene ($J_{2,3} = 5.9$ Hz) [5], thiophene ($J_{2,3} = J_{4,5} = 4.7$ Hz) [4] and selenophene molecules ($J_{2,3} = J_{4,5} = 5.35$ Hz) [4].

It is known that the signals of the α protons in the PMR spectra of five-membered heterocyclic compounds are found at weaker field than the signals of the β protons [6]. The difference in the chemical shifts of the α and β protons in condensed heterocyclic systems decreases; i.e., the electron density in the selenophene ring is equalized (Table 1).

In addition, the signals of the 2 and 3 protons of benzo[b]selenophene and benzo[b]thiophene are shifted to weaker field as compared with the signals of the corresponding protons in selenophene and thiophene as a result of the effect of the ring current in the phenyl ring. One's attention is drawn to the fact that the signals of the 2 and 3 protons in the PMR spectrum of benzo[b]selenophene differ substantially in width. The splitting of the signal of the 3 proton that appears during recording of a rather dilute (about 2%)

TABLE 1. Chemical Shifts of α and β Protons

Compound	δ, ppm		J_{23}, Hz
	$H_{(2)}$ 2-*H*	3-*H*	
Thiophene [4]	7,20	7,08	4,70
Benzo[b]thiophene [5]	7,29	7,26	5,9
Selenophene [4]	7,70	7,12	5,35
Benzo[b]selenophene	7,76	7,36	6,0

TABLE 2. Chemical Shifts of the Protons of a Number of Benzo[b]selenophenes

Substituents	δ, ppm	
	2-*H*	3-*H*
H	7,76	7,36
2-D	—	7,36
3-D	7,36	—
2,3-D_2	—	—
2-CH_3	(2,62)*	7,02
2-CH_3-3D	(2,62)*	—
3-CH_3	7,38	(2,30)*
3-CH_3-2D	—	(2,30)*

*The chemical shifts of the protons of the methyl groups.

solution is evidence for possible spin–spin coupling of it with the protons of the benzene ring with J ~ 0.8 Hz (Fig. 1). This sort of long-range spin–spin coupling is observed in a whole series of aromatic condensed compounds – naphthalene, quinoline, benzo[b]furan, and benzo[b]thiophene [7]. An analysis of the PMR spectra of benzo[b]thiophene [7] and its derivatives [8] demonstrates that this interaction is due to the presence of protons in the 3 and 7 positions,

The intense doublets of the protons of the selenophene ring that are observed in the spectrum of unsubstituted benzo[b]selenophene (Fig. 1) are absent in the PMR spectrum of 2,3-dideuterobenzo[b]selenophene (Fig. 3). A broad singlet from the proton in the 3 position with a chemical shift of 7.31 ppm is clearly seen in the spectrum of 2-deuterobenzo[b]selenophene, while the expected singlet of the unsubstituted proton in the 2 position with a chemical shift of 7.71 ppm (Fig. 3) is clearly evident in the spectrum of 3-deuterobenzo[b]selenophene. As for the assignment of the signals of the protons of the benzene ring in benzo[b]selenophene derivatives, in analogy with the assignment of similar protons in the PMR spectra of benzo[b]thiophene [5], benzo[b]furan [9], and indole [9], they can be divided into two groups – weak-field group A, which contains multiplets of the 4 and 7 protons with a chemical shift of ~7.7 ppm, and strong-field group B, which contains multiplet signals of the 5 and 6 protons with a chemical shift of ~7.1 ppm.

EXPERIMENTAL

3-Deuterobenzo[b]selenophene. A solution of 18.86 g (0.07 mole) of aluminum bromide in 200 ml of absolute ether was added with stirring under nitrogen to 2.52 g (0.28 mole) of lithium deuteride in 50 ml of absolute ether. After 30 min, a solution of 13.8 g (0.07 mole) of selenoindoxyl in 250 ml of absolute ether was added, and the mixture was stirred for 1 h. The mixture was acidified with deuterated acetic acid and stirred for 30 min. The ether was washed with sodium carbonate solution and water. The ether layer was separated and dried with magnesium sulfate. The ether was removed by distillation to give 11.57 g (91%) of 3-deuterobenzo[b]selenophene. The reaction product was purified by chromatography with a column filled with silica gel with elution by petroleum ether (R_f 0.52). After the solvent was removed by distillation, the 3-deuterobenzo[b]selenophene was vacuum-sublimed to give a product with mp 50° (mp 50° [8]).

2-Methyl-3-deuterobenzo[b]selenophene. This compound [8.5 g (86%)] was obtained in the same way from 10.55 g (0.05 mole) of 2-methylselenoindoxyl after vacuum sublimation (mp 61° [1]).

2-Deuterobenzo[b]selenophene. A total of 40 ml (0.375 mole) of n-butyl bromide was added dropwise at 0° to 5.25 g (0.75 mole) of finely cut lithium in 250 ml of absolute ether. After 1 h, a solution of 13.6 g (0.075 mole) of benzo[b]selenophene in 100 ml of absolute ether was added at −70°. The mixture was stirred at the same temperature under nitrogen for 30 min, without cooling for 1 h, and heated and refluxed for 15 min. Deuterated acetic acid [from 18.9 ml (0.187 mole) of acetic anhydride and 5.65 ml (0.28 mole) of deuterium dioxide] was added at −70°. The mixture was stirred without cooling at 36° for 1.5 h. The ether solution was washed with water and dried with magnesium sulfate, and the ether was removed by distillation to give 11.5 g (84%) of 2-deuterobenzo[b]selenophene. The reaction product was purified with a column filled with silica gel with elution by petroleum ether (R_f 0.52). The solvent was removed, and the residue was vacuum-sublimed to give a product with mp 50°.

3-Methyl-2-deuterobenzo[b]selenophene. This compound [4.5 g (76%)] with bp 131° (13 mm) and n_D^{20} 1.6570 was obtained in the same way as 2-deuterobenzo[b]selenophene from 6 g (0.03 mole) of 3-methylbenzo[b]selenophene.

2,3-Dideuterobenzo[b]selenophene. This compound [6.6 g (72%)] with mp 50° (after vacuum sublimation) was obtained from 9.1 g (0.05 mole) of 3-deuterobenzo[b]selenophene via the method described for the preparation of 2-deuterobenzo[b]selenophene.

The PMR spectra were measured with a C-60 HL (JEOL) spectrometer with an operating frequency of 60 MHz. The double resonance spectra were measured with a Varian T-60 spectrometer. All of the spectra were recorded from 10% solutions in CCl_4 with hydromethyldisiloxane as the internal standard.

The chemical shifts of benzo[b]selenophene (δ scale) presented in Tables 1 and 2 were obtained by the addition of 0.05 to the chemical shift relative to hydromethyldisiloxane.

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