The vibrational spectra of thiophene derivative sulfones have been studied. The weakening of the aromatic properties of the thiophene ring in thiophene derivative sulfones is clearly manifested in their vibrational spectra.

Five-membered unsaturated ring compounds containing hetero atoms (e.g., furan, thiophene, pyrrole, and selenophene) have aromatic properties but substantially weakened diene properties. Thus, of the four ring compounds listed above only furan is able to take part in diene synthesis reactions [1]. The aromatic properties of these ring compounds are usually attributed to the participation of the unshared pair of hetero atom electrons with \( \pi \)-electrons in forming the double bonds of a stable aromatic sextet. In this case those transformations of heterocyclic compounds which involve the unshared pair of hetero atom electrons and affect their interaction with the \( \pi \)-electrons of the ring double bonds must of necessity weaken the aromatic properties, and, generally speaking, augment the diene properties of the compound. It is interesting to note in this connection that strong acids interact with pyrrole to form unstable, rapidly polymerizing products [2].

We were interested in determining how the changes in the donor properties of the hetero atom were reflected in the vibrational spectra. The objects of our study were thiophene derivatives and their sulfones. For comparison we also investigated divinyl sulfide, divinyl sulfoxide, and divinyl sulfone.

In contrast to the initial thiophene derivatives, thiophene sulfones have definite diene properties: they react with maleic anhydride and lose the ability to replace the hydrogen atoms in the 3 and 4 positions of the ring by halide atoms or by the acyl radical [1, 3].

The vibrational spectra of sulfones are dealt with in several papers [4–6]. It has been found that the positions and intensities of the S-O bands are practically independent of the nature of the substituents [6]. The vibrational spectra of thiophene derivative sulfones have not been studied previously.

**Experimental Procedure**

The IR absorption spectra were measured using IKS-15 and Leitz spectrometers. The Raman scattering spectra of the liquids were obtained with an ISP-51 spectrograph. The procedure used in obtaining and measuring the RS spectra was described in an earlier paper [7]. The total intensities were measured by direct photometry of the line contours and were plotted on a scale where the \( I_{\text{max}} \) of the \( \Delta \nu = 802 \text{ cm}^{-1} \) line of cyclohexane was taken to represent 500 units. The powder spectra were obtained with a DFS-12 spectrometer.

**Divinyl sulfide.** Method of preparation: dehydration of thiodiglycol and distillation in a fractionating column; purity tested by gas-liquid chromatography (GLC). Boiling point 86°C; \( \delta_{\text{D}}^{\text{H}} 1.5091; \delta_{\text{D}}^{\text{D}} 0.9142 \). (According to [8]: boiling point 42.5°C (150 mm Hg), \( \delta_{\text{D}}^{\text{D}} 1.5076 \).) RS spectrum, * \( \Delta \nu \) (cm\(^{-1} \)): 227 (30, b**), 366 (75), 394 (110), 457 (30), 683 (40), 723 (130), 735 (50, b), 876 (30, b), 965 (10, b), 1042 (105, b), 1218 (5), 1266 (30), 1280 (220), 1322 (25), 1383 (380, b), 1486 (5), 1584 (640), 1598 (480), 2946*** (1), 3007 (6), 3031 (2), 3092 (4).

**Divinyl sulfoxide.** Method of preparation: addition of divinyl sulfide to a 27% solution of hydrogen peroxide in ice-cold acetic acid at -20°C followed by dilution in water and extraction with chloroform; yield: 44%; the product was separated by distillation in a fractionating column; the purity was tested by GLC. Boiling point 59°C/5.5 mm Hg; \( \delta_{\text{D}}^{\text{D}} 1.5149; \delta_{\text{D}}^{\text{D}} 1.0837 \). (According to [9]: boiling point 61°C/4 mm Hg, \( \delta_{\text{D}}^{\text{D}} 1.5143 \).) RS spectrum, \( \Delta \nu \) (cm\(^{-1} \)): 221 (75, b), 263 (55), 314 (90, b), 378 (85), 481 (30), 633 (80), 689 (30), 700 (10), 937 (25, b), 988 (50, b), 1059 (70, b), 1281 (100, b), 1369 (190), 1384 (20), 1608 (420, s) 2950 (2), 3008 (7), 3031 (2), 3092 (4).

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*The IR spectra of divinyl sulfide, divinyl sulfoxide, and divinyl sulfone were not studied.

**Abbreviations: b = broad, s = sharp, d = double.

***Band intensities in the frequency range of the valence vibrations of CH are given on the basis of a visual 10-point scale."
Divinyl sulfone. Method of preparation: same as for the sulfoxide, but with the use of a four-fold excess of perhydrol followed by heating in a boiling water bath; yield: 27%; the product was separated by distillation in a fractionating column; the purity was tested by GLC. Boiling point 65°C/1 mm Hg; n D 1.4772; d D 1.1786. (According to [9]: boiling point 104-105°C/10 mm Hg, n D 1.4772, d D 1.1781.) RS spectrum, Δν (cm⁻¹): 265 (130, b), 385 (120, b), 442 (30), 483 (10), 715 (70), 792 (10), 1010 (40, b), 1125 (150), 1256 (45), 1312 (15), 1386 (120), 1600 (220), 2925 (0), 2968 (3), 3022 (6), 3056 (3), 3104 (4).

2, 5-Di-tert-butylthiophene. Prepared by the method of [10] and separated by distillation in a fractionating column; purity was tested by GLC. Boiling point 69°C/1 mm Hg; n D 1.4924. (According to [10]: boiling point 221-222°C/1.4923.) RS spectrum, μ (cm⁻¹): 165 (120, b), 250 (50, b), 322 (30), 335 (30), 390 (9), 425 (20), 524 (20), 594 (15), 640 (10), 676 (170, s), 698 (5), 712 (5), 783 (5), 791 (20, s), 816 (50), 867 (10), 926 (55, b, d), 965 (5), 990 (5), 1029 (10, b), 1031 (15), 1084 (5), 1104 (20), 1107 (15), 1200 (60), 1228 (25), 1235 (25), 1254 (15), 1316 (30), 1366 (15), 1395 (15), 1411 (150), 1461 (130), 1490 (200), 1543 (25), 2862 (70), 2901 (190), 2927 (145, s), 3067 (30), 3102 (20). The total intensity of the 1575 cm⁻¹ band was measured with a DFS-12 spectrometer in a 25.4% acetonitrile solution and turned out to be 4000 (adjusted for a 100% solution). IR spectrum, ν (cm⁻¹) (Fig. 2): 670, 692, 719, 743, 755, 766, 770, 815, 864, 936, 947, 1045, 1057, 1118, 1141, 1190, 1260, 1278, 1330, 1359, 1368, 1465, 1477, 1494, 1496, 1590, 1700, 1730.

Benzothiophene. Prepared by the method of [11]; not specially purified. RS spectrum coincided with that given in [12].

Benzothiophene sulfone. Prepared by oxidizing benzothiophene with perhydrol in ice-cold acetic acid. Melting point 143°C (after recrystallization from a chloroform + n-octane mixture). (According to [13]: melting point 142-143°C.) RS spectrum, Δν (cm⁻¹): 382 (2), 1035 (1), 1200 (3), 1545 (3), 1595 (5), IR spectrum, υ (cm⁻¹) (Fig. 2): 670, 692, 719, 751, 766, 790, 815, 864, 936, 947, 1045, 1057, 1118, 1141, 1190, 1260, 1278, 1330, 1359, 1368, 1537, 1700, 1790.

3-Methylbenzothiophene.** Prepared by Gaertner’s method [14]. Boiling point 108-110°C (12-14 mm Hg), n D 1.6248. (According to [13]: boiling point 63-72°C/0.3 mm Hg, n D 1.6268, d D 1.137.) RS spectrum, Δν (cm⁻¹): 380 (3), 502 (1), 705 (2), 1014 (2), 1316 (1), 1350 (3), 1527 (3), 1564 (2), 1693 (3). IR spectrum, υ (cm⁻¹) (Fig. 3a): 751, 760, 820, 833, 849, 932, 969, 986, 1019, 1055, 1067, 1086, 1122, 1138, 1158, 1183, 1215, 1262, 1322, 1534, 1584, 1430, 1454, 1540, 1610.

3-Methylbenzothiophene sulfone. Prepared in the same way as benzothiophene sulfone. Melting point 143°C (after recrystallization from alcohol). (According to [15]: melting point 146-146.5°C.) RS spectrum, Δν (cm⁻¹): 380 (3), 1025 (3), 1200 (4), 1300 (3), 1350 (4), 1460 (2), 1580 (5), 1620 (9). IR spectrum, υ (cm⁻¹) (Fig. 3b): 720, 760, 770, 841, 885, 956, 998, 1032, 1107, 1140, 1185, 1215, 1292, 1340, 1570, 1618.

*The RS spectra of the crystalline compounds and 3-methylbenzothiophene were studied with a DFS-12 instrument; the intensities were measured on a 10-point scale.

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