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VIBRATIONAL SPECTRA AND STRUCTURE OF THIOPHENE DERIVATIVE SULFONES

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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 π-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 π-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_{∞}^{M} of the $\Delta\nu$ 802 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; n_D^{20} 1.5091; d_4^{20} 0.9142. (According to [8]: boiling point 42.5° C (150 mm Hg), n_D^{20} 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 (330, 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; n_D^{20} 1.5149; d_4^{20} 1.0837. (According to [9]: boiling point 61° C/4 mm Hg, n_D^{20} 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), 1251 (100, b), 1369 (190), 1384 (20), 1603 (420, s) 2950 (2), 3008 (7), 3040 (4), 3090 (5).

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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^{20} 1.4772; d_4^{20} 1.1786. (According to [9]: boiling point 104–105° C/10 mm Hg, n_D^{20} 1.4772, d_4^{20} 1.1781.) RS spectrum,* $\Delta\nu$ (cm^{-1}): 265 (130, b), 385 (120, b), 442 (30), 483 (10), 715 (70), 952 (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/3 mm Hg; n_D^{20} 1.4924. (According to [10]: 221-222° C, n_D^{20} 1.4923.) RS spectrum, $\Delta\nu$ (cm^{-1}): 165 (120, b), 250 (50, b), 322 (30), 335 (30), 390 (5), 425 (10), 453 (20), 524 (20), 594 (15), 608 (10), 640 (5), 676 (170, s), 693 (20), 712 (5), 741 (25), 763 (5), 791 (20, s), 816 (50), 867 (10), 926 (55, b, d), 965 (5), 990 (5), 1029 (10, b), 1037 (15), 1084 (5), 1104 (20), 1187 (15), 1200 (60), 1235 (25), 1254 (15), 1316 (30), 1366 (15), 1390 (30, s), 1441 (95), 1461 (130), 1490 (200), 1543 (25), 2862 (70), 2901 (190), 2927 (145, s), 2964 (360), 3067 (30), 3102 (20). The total intensity of the 1490 cm^{-1} band was measured with a DFS-12 relative to the 1600 cm^{-1} line of toluene (I = 310) and turned out to be equal to 1100. IR spectrum, ν (cm^{-1}) (Fig. 1a): 739, 797, 816, 823, 835, 868, 922, 935, 993, 1022, 1039, 1056, 1070, 1187, 1200, 1228, 1238, 1257, 1367, 1395, 1463, 1477, 1494, 1546, 1590, 1730.

2, 5-Di-tert-butylthiophene sulfone. Obtained by the method of [10]. Boiling point 127°C (after recrystallization from a chloroform + n-octane mixture). (According to [10]: boiling point 127°C) RS spectrum, $\Delta\nu$ (cm^{-1}): 240 (2), 288 (1), 390 (2), 540 (2), 650 (4), 810 (2), 927 (1), 997 (1), 1115 (1), 1130 (2), 1250 (1), 1280 (2), 1575 (10). 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. 1b): 718, 743, 755, 795, 823, 848, 870, 895, 902, 935, 955, 1010, 1038, 1053, 1063, 1130, 1190, 1280, 1572, 1635, 1705.

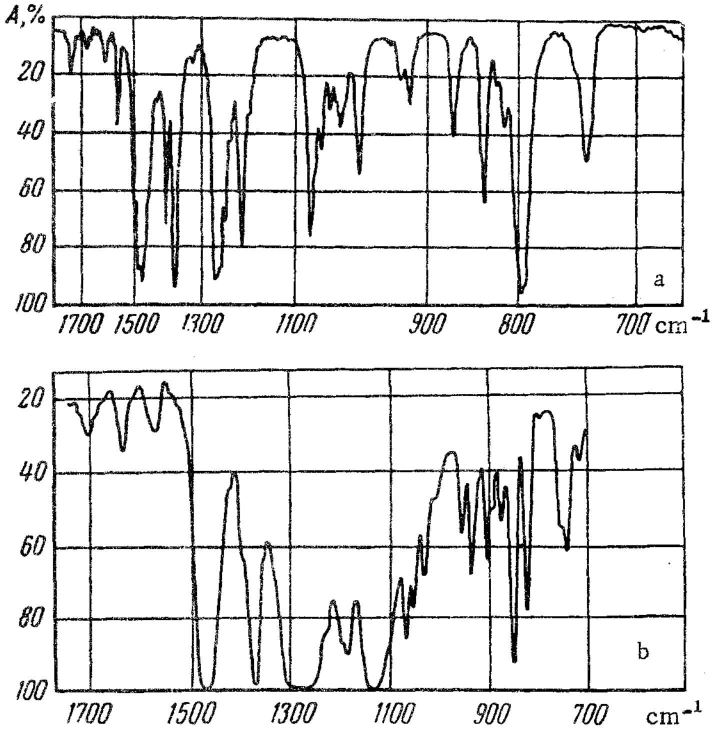

Fig. 1. IR absorption spectra of 2, 5-di-tert-butylthiophene (a, Leitz spectrophotometer, layer thickness: 0.01 mm) and 2, 5-di-tert-butylthiophene sulfone in liquid petrolatum (b, IKS-15 spectrophotometer).

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, $\Delta\nu$ (cm^{-1}): 382 (2), 1035 (1), 1200 (3), 1545 (3), 1595 (5), IR spectrum, ν (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^{20} 1.6248. (According to [13]: boiling point 63-72° C/0.3 mm Hg, n_D^{20} 1.6268, d_4^{20} 1.137.) RS spectrum, $\Delta\nu$ (cm^{-1}): 390 (2), 502 (1), 705 (2), 1014 (2), 1316 (1), 1350 (3), 1527 (3), 1564 (2), 1593 (3). IR spectrum, ν (cm^{-1}) (Fig. 3a): 751, 760, 820, 833, 849, 932, 969, 986, 1019, 1055, 1067, 1086, 1122, 1138, 1158, 1183, 1215, 1262, 1322, 1354, 1384, 1430, 1454, 1540, 1610.

3-Methylbenzothiophene sulfone. Prepared in the same way as bezothiophene sulfone. Melting point 143°C (after recrystallization from alcohol). (According to [15]: melting point 146–146.5°C.) RS spectrum, $\Delta\nu$ (cm^{-1}): 380 (3), 720 (2), 1025 (3), 1200 (4), 1300 (3), 1350 (4), 1460 (2), 1590 (5), 1620 (3). IR spectrum, ν (cm^{-1}) (Fig. 3b): 720, 760, 770, 841, 885, 956, 998, 1032, 1107, 1140, 1185, 1215, 1292, 1340, 1570, 1618.

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*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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Discussion of the Results

The intensities of the double bond lines in the RS spectrum of divinyl sulfide are high. They are considerably higher than the usual values for olefins with isolated double bonds (I_∞ per C=C bond: ~300—500 units [16] Table 1). According to the literature, this is a common characteristic of the spectra of compounds which have a sulfur atom associated with the double bond [17]. The elevated intensity is apparently due to the dynamic interaction of the sulfur atom with the double bond. In the case of divinyl sulfide, the superposition of an additional effect due to the interaction of double bonds by was of the sulfur atom is theoretically possible. This effect cannot be substantial here, however, since, according to the literature, conjugation is not transmitted by sulfur (e.g., see [18]).

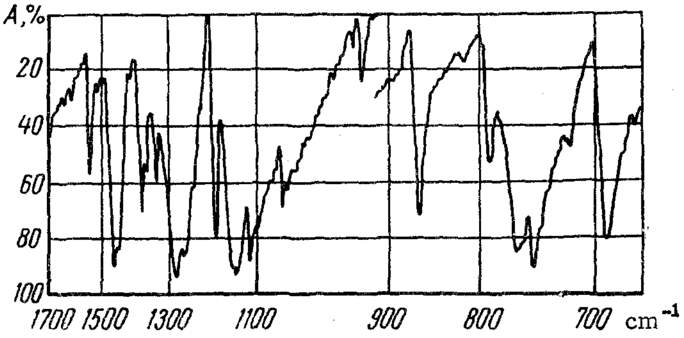

Fig. 2. IR absorption spectra of benzothiophene sulfone in vaseline oil (Leitz spectrophotometer).

The intensities of the ν C=C lines of divinyl sulfoxide and sulfone are considerably lower than those of divinyl sulfide, reaching values typical for olefins with isolated double bonds. This effect can be qualitatively attributed to the weaker interaction of the double bonds with the -SO- and -SO_2- groups in these compounds as compared with sulfides.

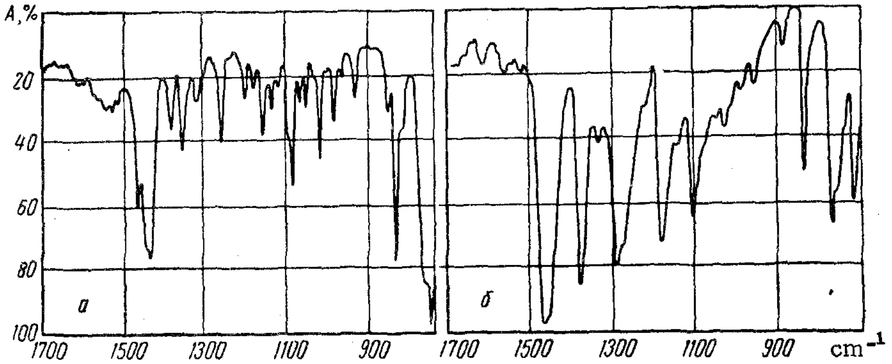

Fig. 3. IR absorption spectra of 3-methylbenzothiophene (a, IKS-15 spectrophotometer, capillary layer) and 3-methylbenzothiophene sulfone in vaseline oil (b, IKS-15 spectrophotometer).

A different state of affairs exists in connection with the spectra of thiophene derivatives and their sulfones. Thus, the conversion of 2, 5-di-tert-butylthiophene into the corresponding sulfone produces a substantial (four-fold) intensification of the symmetric valence vibration line of the ring double bonds with a concomitant increase of almost 100 cm^{-1} in its frequency. The natural explanation for this increase in intensity is that formation of the sulfone weakens the interaction of the sulfur atom with the multiple bonds, since the electrons of the sulfur atom are pulled toward the oxygen atoms. For a cyclic aromatic system this means partial or complete disruption of the aromatic sextet. Under these conditions the thiophene ring must begin to approximate ordinary cyclic dienes with their characteristically high $\nu_{C=C}$ intensities. The similarity of 2, 5-di-tert-butylthiophene sulfone is likewise manifested in the elevation of the frequency $\nu_{C=C}$ to values typical for cyclic dienes [19].

Table 1

Intensities of the $\nu_{C=C}$ Lines in the RS Spectra of Divinyl Sulfide and Its Oxygen Derivatives

Compound	Total intensity of the $\nu_{C=C}$ line	$\frac{I_{\nu_{C=C}}}{(I_{\nu_{C=C}})_{\text{mono-olefins}}}$
C=C—S —C=C	2400	3*
$C{=}C{-}\overset{O}{\overset{\uparrow}{S}}{-}C{=}C$	840	1*
$C{=}C{-}\overset{O\ \ O}{\overset{\nwarrow\nearrow}{S}}{-}C{=}C$	700	1*
Olefins with isolated double bonds	300—500*	1
R—S—C=C [17]	—	1.5
$R{-}\overset{O\ \ O}{\overset{\nwarrow\nearrow}{S}}{-}C{=}C$ [20]	—	1

*Per double bond.

Qualitatively similar results were obtained in studying the RS spectra of benzothiophene, 3-methylbenzothiophene, and their sulfones. Unfortunately, direct measurement of the line intensities was prevented by technical difficulties. A sufficiently clear result was obtained indirectly, however. As we know, upon conjugation with a multiple bond the intensity of the ~1000 cm^{-1} line in the spectra of substituted benze compounds increases relatively little (1.5—2.0 times), while the intensity of the ~1600 cm^{-1} line is not high to begin with. Hence, by measuring the ratio of intensities of the ~1600 and ~1000 cm^{-1} lines one can draw qualitative conclusions about the participation of the benzene bond in the conjugation. Comparison of the parameters of the ~1600 and ~1000 cm^{-1} lines in the spectra of indan, indene, and benzothiophene indicates (Table 2) that by virtue of the partially aromatic properties of the thiophene ring, benzothiophene occupies an intermediate position between indan and indene. Thus, changes in the aromatic properties of the thiophene ring of benzothiophene and its derivatives become noticeable upon comparison of the ratios $I_{\sim1600}/I_{\sim1000}$ with the corresponding values for indan and indene. The data obtained indicate (Table 2, Fig. 4) that the ratios $I_{\sim1600}/I_{\sim1000}$ for benzothiophene and 3-methylbenzothiophene are much smaller than for their sulfones. From this we can conclude qualitatively that benzothiophene sulfones are characterized by weakened aromatic properties of their thiophene ring.

Table 2

Total Intensities of the ~1600 and ~1000 cm^{-1} Lines in the RS Spectra of Benzothiophene and its Derivatives

Line	Indan*	Indene	Benzothiophene	Benzothiophene sulfone**	3-Methylbenzothiophene	3-Methylbenzothiophene sulfone
1000 cm^{-1}	720	1040	1040	—	—	—
1600 cm^{-1}	320	2100	1000	—	—	—
$\frac{I\sim1600}{I\sim1000}$ ratio	~0.4	~ 2	~ 1	($\geqslant$ 2)	~ 1	~ 2

*The indan line intensities were taken from [16] and adjusted for one mole.

**The RS spectrum of benzothiophene sulfone did not exhibit a distinct ~1000 cm^{-1} line, although the ~1600 cm^{-1} line was rather intense. An estimate showed the $I_{\sim1600}/I_{\sim1000}$ ratio to be at least two.

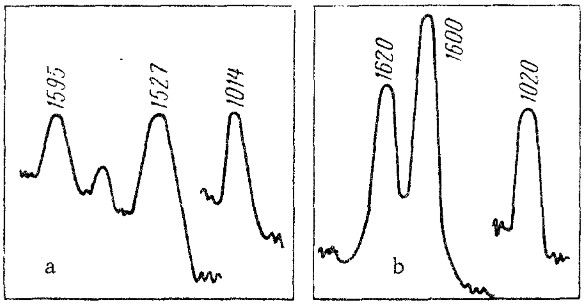

Fig. 4. RS spectra of 3-methylbenzothiophene (a) and 3-methylbenzothiophene sulfone (b) (DFS-12 spectrometer).

Our study therefore shows that the weakening of the aromatic properties of the thiophene ring in thiophene derivative sulfones noted in chemical studies is clearly manifested in their vibrational spectra.

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