STUDIES IN THE FIELD OF ORGANIC METALS

5.* ELECTRICAL CONDUCTION IN COMPLEXES OF 5,5'-DISUBSTITUTED DIBENZOTETRAHYDROTETRATHIAFULVALENES WITH TIN CHLORIDE

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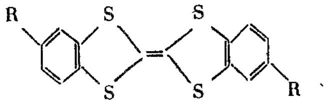
In attempting to synthesize organic compounds which would contain chains of organic and inorganic ions [2] and possess metallic properties we have, in our earlier work, reacted dibenzotetrahydrotetrathiafulvalene (DBTTF) (Ia) with $SnCl_4$ to obtain a highly conductive $(DBTTF)_8(SnCl_6)_3$ complex consisting of regularly arranged stacks of (Ia) molecules and regularly arranged chains of $(SnCl_6)^{2-}$ anions [3].

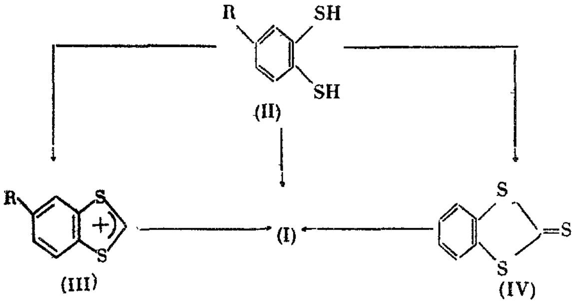
The present work involved the synthesis of derivatives of (Ia) with methyl and alkoxyl substituents in the 5,5' positions, followed by a study of the effect of such substitution, on the reactions with $SnCl_4$ and on the properties of the compounds formed in these reactions.



(I)

R = H(a), Me(b), OMe(c), OEt(d)

There are, in principle, three different procedures available for synthesizing type-(I) DBTTF systems: the interaction of arylene-1,2-dithiols (II) with tetrachloroethylene [4], the interaction of tert-amines with 4,5-aryleno-1,3-dithiolium salts (III), themselves prepared by the reaction of arylene-1,2-dithiols with HCOOH [5], and the interaction of trialkyl phosphites with 4,5-arylenedithiol-1,3-thione-2 (II), themselves formed by reacting 1,2-dithiols with CS_2 [6].



The key compound in each of these reactions, arylene-1,2-dithiol (II), is generally prepared from substituted 2-aminobenzenesulfonic acids, following a lengthy process [7] which begins with sulfonation of a substituted aniline.

Attempts to carry out the direct sulfonation of 4-alkoxyaniline-2-sulfonic acid by the method of [8] were unsuccessful. We have developed a new procedure for synthesizing the substituted 2-aminobenzenesulfonic acids in which one starts by carrying out Meerwein reactions with the substituted 2-nitroanilines (Va, b) [9].

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*For previous communication see [1].

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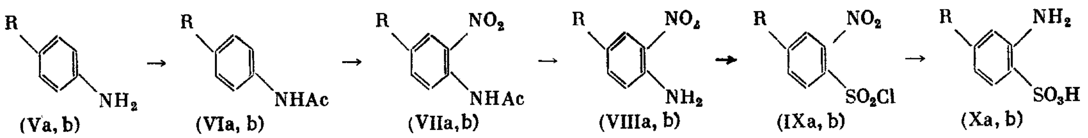
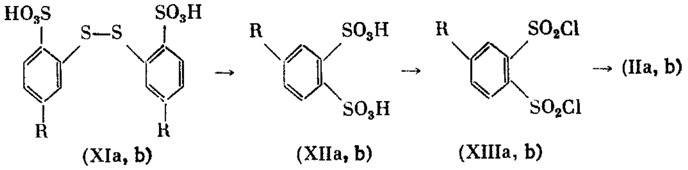
TABLE 1

Product complex	Starting compound	Ratio, (Ia)-(Id): $SnCl_4$ (molar)	Solvent	σ, 1/Ω·cm (pellets)
$(Ia)_8(SnCl_6)_3$ (XIV)	(Ia)	1 : 10	Acetonitrile	0,7
$(Ib)_6Sn_2Cl_{10}$ (XV)	(Ib)	1 : 10	»	$5\cdot10^{-2}$
$(Ic)_6Sn_2Cl_{10}$ (XVI)	(Ic)	1 : 2	»	$6\cdot10^{-2}$
$(Id)_6Sn_2Cl_{10}$ (XVII)	(Id)	1 : 3	»	$3\cdot10^{-2}$
$(Ie)_2Sn_2Cl_{10}$ (XVIII)	(Ie)	1 : 10	Benzene	$1\cdot10^{-4}$



R = MeO (a), EtO (b).

The 4-alkoxy-2-aminobenzenesulfonic acids (Xa, b) obtained here were converted into 5,5'-dialkoxydiphenyldisulfide-2,2'-disulfonic acids (XIa, b) by a Leuckart reaction, oxidized to the corresponding 4-alkoxybenzene-1,2-disulfonic acids (XIIa, b), and then converted into the 4-alkoxybenzene-1,2-disulfonyl chlorides (XIIIa, b) in the usual manner [10].



The latter were then reduced to the 4-alkoxybenzene-1,2-dithiols (IIa, b) by the action of metallic Sn in concentrated HCl, the yield being 70% without dealkylation [11].

The 5,5'-dialkoxydibenzotetrahydrotetrathiafulvalenes (Ia, b) were prepared from the benzodithiolium salts (III) and from the benzodithiolthiones (IV), the yield in both cases being the order of 30%. The structure of (I) was confirmed, first by elementary analysis and then by comparison of the electronic spectra of (I) and the corresponding thiones (Fig. 1).

The complexes obtained by the interaction of (Ib)-(Id) with $SnCl_4$ are not of the same type as those obtained by the interaction of (Ia) with $SnCl_4$ (Table 1). The electronic spectra of compounds (XIV)-(XVII) show bands corresponding to absorption by the neutral molecules (Ia)-(Id) and their radical anions, the maxima in

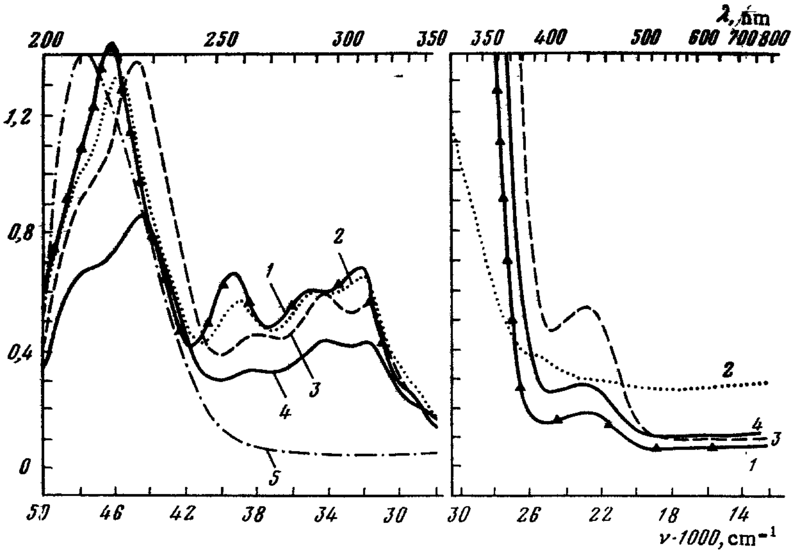


Fig. 1. Electronic spectra of acetonitrile solutions of 5,5'-disubstituted tetrahydrotetrathiafulvalenes: 1) (Ia); 2) (Ib); 3) (Ic); 4) (Id).

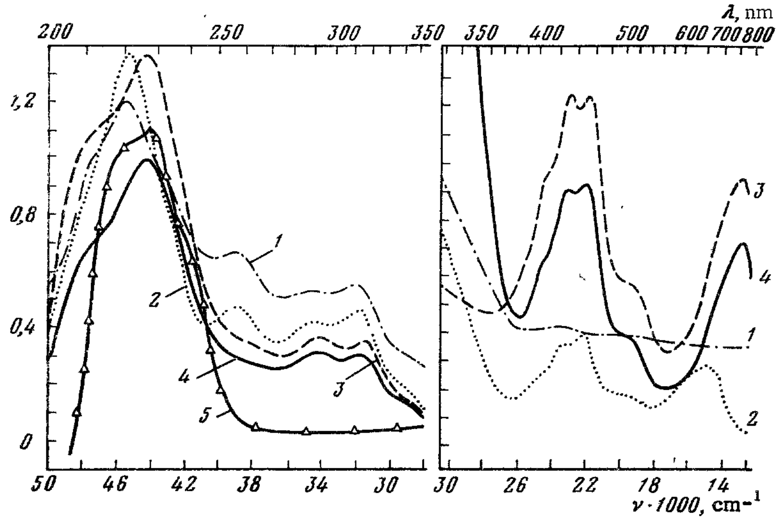


Fig. 2. Electronic spectra of CH_3CN solutions of complexes of 5,5'-disubstituted tetrahydrotetrathiafulvalenes with $SnCl_4$: 1) (XIV); 2) (XV); 3) (XVI); 4) (XVII).

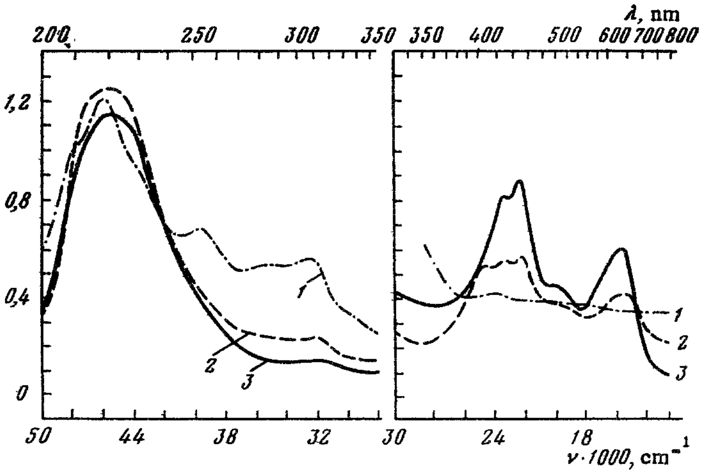


Fig. 3. Electronic spectra of CH_3CN solutions of complexes of 5,5'-disubstituted tetrahydrotetrathiafulvalenes with $SnCl_4$: 1) (XIV); 2) (XVIII) (in nitrobenzene); 3) (XVIII) (in benzene).

the radical cation bands being shifted toward longer wavelengths (679.9, 762, and 768 nm, respectively), just as would be anticipated (Fig. 2). The electronic spectra of compound (XVIII) shows only the radical cation bands for (Ia) (Fig. 3).

The IR spectra of the solids (XV)-(XVIII) each show a characteristic band at 320 cm^{-1}, this being assigned to the Sn–Cl bond in the complex anion. The appearance of an ESR signal with a g factor of approximately 2 confirmed the existence of radical cations in the solids (XV)-(XVIII).

Studies of Mössbauer spectra showed the value of f', the probability of resonance absorption, to be essentially equal to zero in these systems at 300°K. The results obtained from spectra developed at 80°K are shown in Table 2. The parameter values are much the same, for $(NH_4)_2SnCl_6$ and for compound (XIV) in which the Sn atom is octahedrally surrounded, being affected but little by the type of cation in question. It is true, however, that the value of f' is two orders lower in the case of compound (XIV), the presence of the large cation making for looseness in the lattice packing.

The spectra of compounds (XV) and (XVIII), the latter in both benzene and nitrobenzene solution, consist of two monolines of identical areas. The parameters of the first of these lines are close in value to the parameters of the octahedrally surrounded Sn in $[SnCl_6]^{2-}$. The parameters of the second line have essentially the

TABLE 2

Compound	Type of spectrum	Line parameters* Γ(δ)	Value of f, %	Valence state of Sn
$(NH_4)_2SnCl_6$	Monoline	0,98 (−1,5)	1,3	+4
(XIV)	»	0,83 (−1,57)	0,74	+4
(XV)	Two monolines	0,80 (−1,52)	$f_1' : f_2' = 1 : 1$	+4
(XVI)	The same	0,84 (−1,44)	$f_1' : f_2' = 1 : 1$	+4
(XVIII)	»	0,86 (−1,50)	$f_1' : f_2' = 1 : 1$	+4

*Γ designates the line width in mm/sec; δ is the chemical shift in mm/sec. For the second monoline: (XV) 0.80 (−1.92); (XVI) 0.84 (−1.99); (XVIII) 0.86 (−1.97).

same value in all three cases, and probably characterize a second Sn(IV) coordination with a purely inorganic environment, the same in each case. In the case of compound (Ia) it seems clear that reaction leads largely to formation of the $(SnCl_6)^{2-}$ anion [3]; this coordinates with the (Ia) to give the (XIV) complex which precipitates out of the acetonitrile solution leaving the Sn^{2+} anion behind (qualitative reaction).

The introduction of electron-donor substituents, even those as weak as the CH_3 group, into the molecule of (I), or a change of solvent in the reaction system, leads to the formation of an anion containing two Sn(IV) atoms in different types of ligand environments. The data of the elementary analysis suggested that this anion consists of (Sn_2Cl_{10}) fragments, the latter so constructed that one of the Sn atoms is in an octahedron and the other in a tetrahedron, pyramid, or trigonal bipyramid which shares a Cl atom with the octahedron. The cationic part of molecules (XV)-(XVIII) is a regularly packed column of molecules (Ib)-(Id), each (Sn_2Cl_{10}) fragment being probably accompanied by two radical cations and four neutral molecules. The cation of the (XVIII) molecule probably contains only radical cations, the failure of the electronic spectra to show evidence of the neutral (Ia) molecule suggesting complete charge transfer from the (Ia) molecule to the anion.

The conductivity (σ) of these compounds is in line with the above remarks: in compounds (XV)-(XVIII), where the transfer of the electron from the donor molecule (Ib)-(Id) to the acceptor is incomplete, $\sigma \approx 5 \cdot 10^{-2}$ $1/\Omega \cdot cm$, whereas in compound (XVIII), where the electron transfer is presumably complete and the molecular column consists only of (Ia) radical cations, $\sigma = 1 \cdot 10^{-4}$ $1/\Omega \cdot cm$.

From this it can be concluded that the introduction of electron-donor substituents into the system must affect the complexing process. The conductivity of these compounds must be affected by the presence of anions other than $[SnCl_6]^{2-}$, and by steric hindrances arising from the introduction of the substituents.

EXPERIMENTAL

The electronic spectra were obtained with a Specord spectrometer, working in acetonitrile solution, the IR spectra with a UR-10 spectrometer, and the Mössbauer spectra with an AE-256 spectrometer, working with tablets containing a mixture of the complex with paraffin. The source was $Ca^{119}SnO_3$ which had been calibrated against $[(C_2H_5)_2SnO]_n$ at 80°K; the line width was 0.81 mm/sec.

4-Methoxy-2-nitrobenzenesulfonyl Chloride (IXa). To 191 g (1.16 mole) of (VII) [12] dissolved in 1260 ml of 24% HCl at 0-5°C there was added, over 1-2 h, 88.5 g (1.28 mole) of $NaNO_2$ dissolved in 206 ml of water. The filtered diazo compound solution was poured directly into a solution containing 860 ml of AcOH, 78 g of $CuCl_2$, and 20 ml of water which had been saturated with SO_2. This led to a violent evolution of N_2; after 20-25 min, the precipitate was filtered off, washed with water, and dried. The yield of (IXa) was 225 g (78%), mp 75-78°C [13].

4-Ethoxy-2-nitrobenzenesulfonyl Chloride (IXb). This compound was synthesized by a procedure similar to that described above; yield 72.5%, mp 76-77°C. Found: C 38.05; Cl 14.45; N 5.38%. $C_8H_8ClO_4$. Calculated: C 38.35; Cl 14.2; N 5.71%.

4-Methoxy-2-aminobenzenesulfonic Acid (Xa). A mixture of 225 g (0.896 mole) of (IXa), 110 g (1.04 mole) Na_2CO_3, and 693 ml water was refluxed for 45 min and filtered; AcOH was added to an acid reaction with litmus, the mixture heated to boiling, 422 g Fe added portionwise over 15 min with constant stirring, and reduction allowed to continue for 4-5 h. The precipitate was filtered off, washed with hot water, and the filtrate cooled to 15°C and acidified with 396 ml concentrated HCl. The precipitate brought down here was washed and dried. Yield of (Xa) 101 g (35%).

4-Ethoxy-2-aminobenzenesulfonic Acid (Xb). This compound was synthesized by a procedure similar to that described above, yield 43%.

4-Methoxy-1,2-benzenedisulfonic Acid (XIIa). A solution containing 34.6 g (0.5 mole) $NaNO_2$ dissolved in 60 ml of water was added over 1 h to the liquid layer of a mixture containing 101 g (0.496 mole) (Xa), 81.5 ml concentrated HCl, and 90 g of ice at 0-5°C, and the whole stirred for 1 h. The crystallized diazo compounds were filtered off and added, portionwise, to a solution containing 88 g (0.51 mole) of KSC(:S)OEt dissolved in 180 ml water at 60-70°C. The resulting mixture was stirred at this same temperature for 2 h, cooled to 50°C; 220 g of $KMnO_4$ was then added and the temperature gradually brought up to 100°C. The excess $KMnO_4$ was then broken down with EtOH. The mixture was then cooled, filtered, evaporated to dryness on the water bath, and the residue dried to constant weight. The yield of the raw sulfonic (XIIa) acid was 195 g.

4-Ethoxy-1,2-benzenedisulfonic Acid (XIIb). This compound was synthesized by a procedure similar to that described above.

4-Methoxy-1,2-benzenedisulfonyl Chloride (XIIIa). A mixture of 131 g raw (XIIa) and 260 g of PCl_5 was heated for 4 h at 120°C, and then poured onto ice. The residue was filtered off and washed with water. Yield of (XIIIa) 39.7 g (32.6%), mp 107-110°C. Found: Cl 22.96%. $C_7H_6Cl_2O_5S_2$. Calculated: Cl 23.21%.

4-Ethoxy-1,2-benzenedisulfonyl Chloride (XIIIb). This compound was synthesized by a procedure similar to that described above. Yield 58.5%, mp 106-107°C [14].

4-Methoxyphenylene-1,2-dithiol (IIa). To 90 g Sn dissolved in 100 ml of concentrated HCl there was added 10 g (0.033 moles) of (XIIIa); the resulting mixture was heated to 60°C, 300 ml of concentrated HCl was added, and the mixture heated for another 2 h at 95°C. The oily product was separated by steam distillation, extracted with ether, and distilled in vacuum. Yield of (IIa) 3.1 g (46%), bp 136-137°C (5 mm). Found: C 48.73; H 4.83; S 36.37%. $C_7H_8OS_2$. Calculated: C 49.1; H 4.72; S 37.35%.

4-Ethoxyphenylene-1,2-dithiol (IIb). This compound was synthesized by a procedure similar to that described above, yield 48%, mp 30-31°C [14].

4,5-(4-Methoxybenzo)-1,3-dithiolium Perchlorate (IIIa). A mixture containing 3 g (0.021 mole) of (IIa) and 86 ml of anhydrous HCOOH was refluxed for 30 min and then cooled to 20°C; to it there was added, dropwise, 7 ml of a 57% solution of $HClO_4$, the mixture was boiled for 10 min, cooled to 20°C, diluted with 220 ml of anhydrous ether, and let stand overnight at ~0°C. The precipitate was then filtered off and washed with anhydrous ether. Yield of (IIIa) 4.2 g (69.4%).

4,5-(4-Ethoxybenzo)-1,3-dithiolium Perchlorate (IIIb). This compound was synthesized by a procedure similar to that described above, yield 72%.

4,5-(4-Methoxybenzo)-1,3-dithiol-2-thione (IIa). To a solution containing 3 g (0.0214 mole) of (IIa) dissolved in 150 ml of 1 N NaOH there was added 15 ml of CS_2 and the mixture refluxed for 2 h, at the end of which time the excess CS_2 was evaporated off. Yield of (IIa) 2.54 g (72%), mp 142-142.5°C. Found: C 44.35; H 2.15; S 44.20%. $C_8H_6OS_3$. Calculated: C 44.80; H 2.83; S 44.80%.

4,5-(4-Ethoxybenzo)-1,3-dithiol-2-thione (IVb). This compound was synthesized by a procedure similar to that described above, yield 90%, mp 120-121°C [14].

5,5'-Dimethoxydibenzotetrahydrotetrathiafulvalene (Ic). Method A. To a solution containing 8.2 g (0.027 mole) of (IIIa) dissolved in 100 ml of anhydrous CH_3CN there was added, dropwise at 20°C, 20 ml of anhydrous Et_3N. The resulting mixture was stirred for 3 h at this same temperature and then allowed to stand overnight at 0°C. The precipitate which had formed at the end of this time was filtered off and washed with CH_3CN. Yield of (Ic) 1.47 g (30%), mp 179-180°C (from CH_3CN). Found: C 52.75; H 3.32; S 35.70%. $C_{16}H_{12}O_2S_2$. Calculated: C 52.90; H 2.98; S 35.21%.

Method B. A mixture containing 1 g (0.005 mole) of (IVa) and 1 ml of $(MeO)_3P$ was refluxed in Ar for 10 h and then allowed to stand overnight. To it there was then added 10 ml of anhydrous CH_3CN and the precipitate filtered off. Yield of (Ic) 10.3 g (32.4%), mp 178-180°C.

5,5'-Diethoxydibenzotetrahydrotetrathiafulvalene (Id). The compound was synthesized by methods similar to A and B described above, yield 29%, mp 186-187°C (from CH_3CN). Found: C 55.45; H 3.71%. $C_{18}H_{16}O_2S_4$. Calculated: C 55.12; H 4.08%. UV spectra (λ, nm (log ε), dioxane): 226 (4.75), 258 (4.17), 290 (4.31), 316 (4.30), 438 (2.47).

Compound (XIV) was synthesized by the procedure of [12], yield 66%.

Compound (XV) was prepared by adding 0.785 g (0.003 mole) of $SnCl_4$ dissolved in 10 ml of CH_3CN to a boiling solution of 0.05 g (0.00015 mole) of (Ib) dissolved in 120 ml of CH_3CN. This procedure gave 0.053 g (80%) of the complex in the form of small violet needles with metallic sheen. Found: C 44.49; H 3.36; S 28.94; Cl 11.90; Sn 9.57%. $C_{96}H_{72}S_{24}Sn_2Cl_{10}$. Calculated: C 44.56; H 2.78; S 29.7; Cl 13.73; Sn 9.20%. UV spectra, visible (λ, nm, CH_3CN): 220.5, 255.2, 287.5, 311.9, 399.4, 422.3, 447.2, 508.1, 672.9.

Compound (XVI) was prepared by a procedure similar to that used for synthesizing (XV), reacting two solutions, one containing 0.05 g ($1.37 \cdot 10^{-4}$ mole) of (Ib) dissolved in 50 ml of CH_3CN and the other 0.071 g ($2.74 \cdot 10^{-4}$ mole) of $SnCl_4$ dissolved in 1 ml of CH_3CN. This gave 0.035 g (55%) of complex (XVI). Found: C 41.2; H 3.24; S 27.25; Cl 11.91; Sn 8.00%. $C_{96}H_{72}O_{12}S_{24}Sn_2Cl_{10}$. Calculated: C 41.48; H 2.59; S 27.65; Cl 12.78; Sn 8.57%. UV spectra (λ, nm, CH_3CN): 209.2, 225.1, 261.8, 290.5, 314.9, 405.4, 429.9, 450.9, 510.2, 762.2.

Compound (XVII) was prepared by a procedure similar to that used for synthesizing (XV), reacting two solutions, one containing 0.1 g ($2.55 \cdot 10^{-4}$ mole) of (Id) dissolved in 100 ml of CH_3CN, and the other 0.199 g ($7.65 \cdot 10^{-4}$ mole) of $SnCl_4$ dissolved in 1.3 ml of CH_3CN. This procedure gave 0.067 g (81%) of the complex in the form of small dark needles. Found: C 43.84; H 3.65; S 25.98; Cl 12.01; Sn 8.02%. $C_{108}H_{96}O_{12}S_{24}Sn_2Cl_{10}$. Calculated: C 44.0; H 3.20; S 26.07; Cl 12.05; Sn 8.08%. UV spectra (λ, nm, CH_3CN): 210.7, 226.1, 292.4, 316.5, 405.8, 430.1, 450.5, 521.4, 768.1.

The authors would like to thank I. G. Gusakovskaya for interpreting the Mössbauer spectra.

CONCLUSIONS

1. Methods of synthesizing the 5,5'-substituted dibenzotetrahydrotetrathiafulvalenes have been developed.

2. Electrically conducting complexes of 5,5'-substituted dibenzotetrahydrotetrathiafulvalenes with tin chloride have been prepared.

3. The introduction of substituents into the dibenzotetrahydrotetrathiafulvalene system during the preparation of these conducting compounds leads to the formation of complexes which differ from the unsubstituted dibenzotetrahydrotetrathiafulvalenes in both composition and conduction.

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