Investigations of the structure of a series of tetrathioethylenes (TTE) \((RS)_2C\equiv C(SR)_2\) at \(R = CH_3\) [1], \(C_6H_5\) [2], trans-CH\(_3\), \(C_6H_5\) [3] in a crystalline state showed that four S atoms of the above molecules are situated in the plane of the ethylene bond, while the R radicals diverge from the plane and have a different mutual orientation.

No structural data are available for tetrasulfonylethylenes. However, the relatively symmetrical structure of the central fragment of these molecules is borne out by the fact that the frequencies of their C=C bond are active in the Raman spectra, and do not appear in the IR spectra [4]; this is also applicable to the vibrational absorption spectra of tetrathioethylenes.

It is known that in aromatic and unsaturated compounds, the S atom may display both \(\pi\)-donor, and \(d\pi\)-acceptor properties with respect to the \(\pi\)-system of electrons of the aromatic (unsaturated) fragment. The most favorable conditions for the \(\pi\)–conjugation of the unshared electron pair of the S atom with a system of \(\pi\)-electrons of the C=C bond are obtained when a planar conformation of the molecules exists, i.e., when the SR groups are present in the plane of the C=C bond. The \(d\pi\)-acceptor properties due to the presence of free \(d\)-orbitals on the S atom are manifested when the conformational limitations caused by possible rotations of the SR groups are practically eliminated.

As a consequence of the aforesaid, it was of interest to ascertain the main factors which determine the observed nonplanar structure of TTE: the effects due to packing of the molecules in the crystal, the effects of the crystalline field, or steric and intramolecular electronic \(d\pi\)-interactions.
To determine whether the conformation of the TTE molecules is retained on transition from the crystal state to solution form, we measured the dipole moments (DM) of several compounds of the following classes: tetrakis(ethylthio)ethylene (C₂H₅S)₂C=C(SC₂H₅)₂ (I), tetrakis(octylthio)ethylene (C₈H₁₇S)₂C=C(SC₈H₁₇)₂ (II) and tetrakis(ethylsulfonyl)ethylene (C₂H₅SO₂)₂C=C(SO₂C₂H₅)₂ (III); (the syntheses (I)-(III) are described in [4, 5]).

In addition, in the present work we continued study of the complexation processes with participation of polyfunctional electron donors. To do this, an evaluation was made of the coordinational properties of the above compounds with respect to Al and Ga halides using calorimetric and dielectrometric methods [6].

The DM of compounds (I) and (II) (Table 1) measured in benzene are practically the same (1.18 and 1.19 D); hence, it can be concluded that the length of the aliphatic radical has substantially no influence on the conformation of the molecule which determine the value of DM. The somewhat lower value of DM of (I) measured in cyclohexane (1.04 D) indicates a certain non-neutrality of benzene as a solvent with respect to similar compounds. The DM of the central fragment of the molecules of C=C studied should be equal to zero according to structural data [1-3], because of relative compensation of the C-S bonds. The most likely reason for the presence of a DM in (I) and (II) is the asymmetry in the disposition of the SR groups with respect to the plane of the central fragment. It is possible that the conformation of the above molecules in the solution is similar to their conformation in a crystal and is characterized by divergence of the SR groups from the plane of the central fragment. The last fact is in accordance with the concept of participation of d-orbitals of the S atom in the τ-electronic interaction as postulated in [7] based on analysis of the electronic spectra of the TTE series. The relatively low value of DM of (III) (2.26 D, Table 1) containing four highly polar sulfonyl groups (~5.0 D [8]) also points to a certain symmetry of their mutual disposition with substantial compensation of the DM.

Investigation of complexation reactions showed that the S atoms in (I) and (II) display electron-donor properties in the reaction with typical electron acceptors – GaCl₃ and AlBr₃. Complexes with a 1:1, 1:2 composition are successively formed, as well as complexes with a more complex stoichiometry, but because of poor solubility (possibly also because of the occurrence of secondary processes), the parameters of the latter could not be established. Tables 1 and 2, respectively, show the values of DM (μ, D) and heats of formation (ΔH, kJ/mole) of complexes with a 1:1 and 1:2 composition, and for comparison parameters of a series of complexes with sulfides are also given. It should be noted that the values of ΔH were obtained from the experimental values of ΔH, by introducing corrections for the energy of dimerization of GaCl₃ (55.0 kJ/mole) [6]. The complexation processes of (I) and (II) are accompanied by a considerable increment in DM, whose value is similar to the increment of DM of GaCl₃ complexes with other sulfides (Table 1). This indicates that the nature of the intermolecular bonds can be identified as of the charge transfer type, which are formed as a result of interaction of the unshared pair of electrons on the S atom and the vacant orbital of the metal atom.

Judging from the values of ΔH of the 1:1 complexes, the electron donor properties of the S atom in TTE are similar to the properties of the S atom of alkyl aryl sulfides (Table