This thesis describes a spectroscopic and theoretical investigation of ions derived from cyclopentadithiophenones, cyclopentadithiophenones and dithienothiophene-dioxides.

In the literature survey (chapter 1) the characteristics of the isomers of each series are discussed. The modes of annelation of the thiophene rings strongly affect the chemical and physical properties.

ESR spectra of radical-anions of cyclopentadithiophenones and the three most aromatic dithienothiophene-dioxides are described in chapter 2. Assignment of the hyperfine splitting constants was based on the hyperfine splitting constants of deuterated derivatives. Deuterium-hydrogen exchange has been observed during the electrolytical generation of some radical-anions. The hyperfine splitting constants of radical-anions of cyclopentadithiophenones are compared with those of dithienyl ketones and an analysis of the preferred conformations of the latter radical-anions is given.

The experimental hyperfine splitting constants are compared with values obtained by Hückel/McLachlan calculations (chapter 3). The thiophene sulfur atoms are treated using a model in which only the 3p-orbitals participate in the $\pi$-system (p-model) and a model in which the vacant 3d-orbitals participate as well (d-model). Calculations performed with the d-model for sulfur afford an adequate pre-
diction of the experimental spin-density distributions in the radical-anions of cyclopentadithiophenones. The agreement obtained with the p-model for sulfur in these radical-anions is poorer. This outcome contrasts with results of investigations reported in the literature. No decision can be made about the preferability of a p- or d-model on the basis of correlation of the polarographic half wave reduction potentials of cyclopentadithiophenones (chapter 2) with the calculated energies of the lowest vacant MO (chapter 3). Both p- and d-model give a good prediction of the experimental spin-density distribution in the radical-anions of dithienothiophene-dioxides.

The carbonium ions obtained by dissolving cyclopentadithiophenones and fluorenone in FSO₃H/SbF₅-SO₂ were studied at -60°C by means of NMR spectroscopy (chapter 4). Di- and mono (carbonyl)-protonation occurred. Ring protonation of cyclopentadithiophenones takes place at α-carbon atoms except ketone III that is protonated at the carbocyclic ring. Ketone II and fluorenone are found to be protonated first at the carbonyl group. PPP calculations show that carbonyl protonated ketones II, V and VI are energetically more favorable than carbonyl protonated ketones I, III and V. From the values of the chemical shifts of the =ÖH protons it is concluded that the C-O bond remains largely a double bond. Furthermore, chapter 4 deals with the NMR spectra of cyclopentadithiophenes in CF₃COOH at -15°C. Cyclopentadithiophenes I, IV and VI are protonated at corresponding α-positions in the b-annelated thiophene ring.

The absorption frequencies in the ultraviolet spectra of cyclopentadithiophenes I, IV and VI protonated in CF₃COOH at -15°C are in very good agreement with transition energies calculated by PPP methods (chapter 5). The absorption bands of cyclopentadithiophenones and fluorenone show unusual shifts towards longer wavelengths when the solvent is changed from cyclohexane to CF₃COOH (-15°C). These shifts are attributed to strong hydrogen bond formation between the carbonyl oxygen atom and the solvent. Strong hydrogen bond formation leads to charge displacements in the σ-framework. A model is presented which takes this σ-polarization into account in PPP calculations by modifying the core parameters of the atoms involved. Using this model
a good description is obtained of the experimental transitions in CF₃COOH. In addition, chapter 5 describes the determination of the crystal structure of cyclopentadithiophene I by means of X-ray diffraction. The geometry of the cyclopentadithiophenes and cyclopentadithiophenones used in the PPP calculations was based on data obtained from this structure determination.