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Cyclopentadithiofenen endithienopyridinen synthese en eigenschappen

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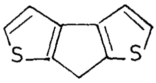
SUMMARY

This thesis deals with the synthesis and properties of cyclopentadithiophene systems and dithienopyridines. In chapter 1 the literature concerning the preparation and properties of the six cyclopentadithiophenes and the six cyclopentadithiophenones (e.g. 1 and 13) is surveyed.



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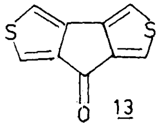

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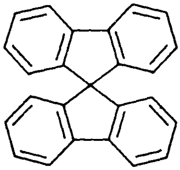
The preparation of these compounds, achieved recently, focussed our attention on the useful insights into spectral characteristics of unsaturated spiranes furnished by the theory of Simmons[19]. Only one isomer of spirobifluorene (17) can exist but the presence of a heteroatom in spiro-conjugated systems of type. 18 and type 19 increases the number of possible isomers to six and twenty-one respectively.



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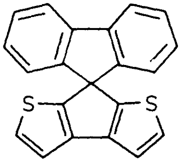

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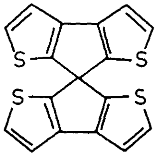

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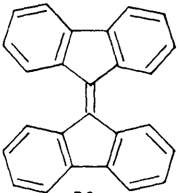
In chapter 2 the preparation of four spiro[cyclopentadithiophene]fluorenes (type 18) is described as well as unsuccessful attempts to prepare spiranes of type 19. The expected bathochromic shift of the longest wavelength bond in the UV spectra of these heterospiranes was clearly evident and is in agreement with Hückel and PPP calculations.

Chapter 3 deals with the synthesis of some thiophene analogues (type 72 and 89) of $\Delta^{9,9'}$ bifluorene (58).



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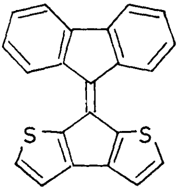

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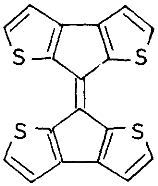

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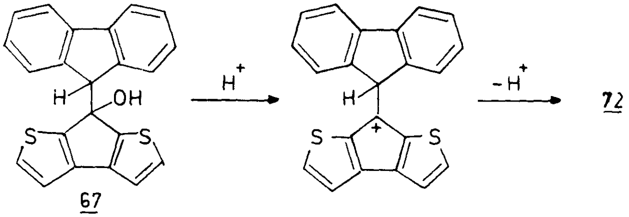
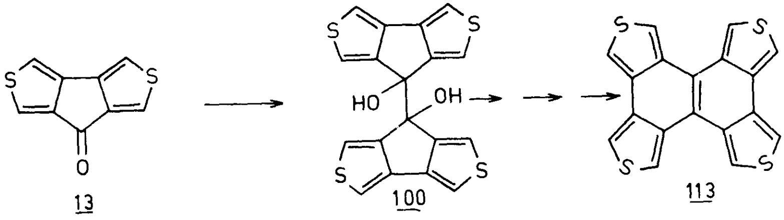
The effect of the possible nonplanarity of these heterofulvenes on the UV, NMR and IR spectra is discussed.

The great difference in reactivity of the intermediate carbinols (e.g. 67) in the dehydration reactions was particularly interesting.



The difference in stability of the six cyclopentadithiophene cations (calculated by Koster), proved the prediction that the more stable the intermediate carbonium ion the easier the dehydration reaction occurs.

In chapter 4 the pinacol reduction of three cyclopentadithiophenones is described (e.g. 13). Due to the annellation of the thiophene rings there was a great difference in yield of the pinacol product.

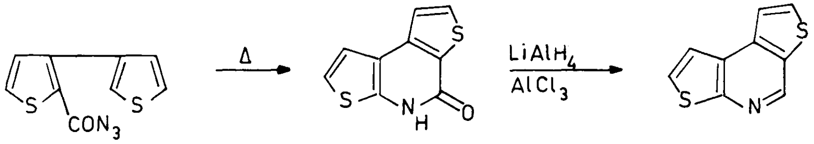


An explanation is given for the fact that the least stable intermediate cyclopentadithiophene radical gave the highest yield on pinacol product.

For isomer 100 the pinacol rearrangement to a spiroketone and the further reaction to a naphthotetrathiophene (113) is described.

Chapter 5 deals with the unsuccessful Beckmann- and Schmidt rearrangement of the cyclopentadithiophenones to the thiophene analogues of phenanthridone.

The successful reaction path leading to three dithienopyridones was found in the cyclisation reactions of the appropriate dithienylazides (e.g. 139).



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The reduction of these dithienopyridones to the dithienopyridines could be achieved by the reaction with a mixture of lithiumaluminiumhydride and aluminium chloride. The UV spectra of these dithienopyridines closely resemble the UV spectra of phenanthridine and the benzodithiophenes