

2 h at room temperature the mixture was evaporated, finally in high vacuum at 40°C. The residue was extracted with ether and filtered through activated charcoal on celite. Concentration and addition of petroleum ether afforded a crystalline product (2.85 g, 84 %), which after recrystallization from ether-petroleum ether had m.p. 130-32°C. (Found: C 56.04; H 7.40; N 12.91. Calc. for $C_{20}H_{31}ClN_4O_2S$: C 56.25; H 7.32; N 13.12.) IR bands (KBr) occurred at 3250, 1650 and 1617 cm^{-1} . NMR signals ($CDCl_3$): S- CH_3 : 2.05, s, 3H. N(CH_3)₂: 2.23, s, 6H. >NCH₃: 2.31, s, 3H. pip(CH_2)₄: 2.47, m, 4H and 3.73, m, 4H. S- CH_2 CH₂-C: ca. 2.30, m, 4H. -C-CH₂-N: ABq 2.93, d, $J=14.5$, 1H and 3.51, d, $J=14.5$, 1H. ClC₆H₄ -: 7.43, d, $J=8.5$, 2H and 7.80, d, $J=8.5$, 2H. -CONH: 8.37, broad s, 1H.

(IIa), hydrochloride (200 mg) was gradually dissolved in *N*-methylpiperazine (5 ml) by heating to 50°. After exhaustive evaporation in high vacuum and work-up as described for (IIIb) an identical compound was obtained.

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Skeletal Rearrangements in Thienothiophenes under Electron Impact

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Recent papers by de Jong *et al.*¹ and by Cooks and Bernasek² have prompted the author to submit his results on the skeletal rearrangements of thieno[2,3-*b*]thiophene (I) and thieno[3,2-*b*]thiophene (II)³ under electron impact. The spectra were recorded on an AEI MS 902 mass spectrometer at 70 eV and at 16 eV. All voltages given are nominal values. The compounds were introduced through the all glass heated inlet system with source temperatures of 230° and 50°, but no significant dependence on the source temperature was observed. The major fragments were examined at high resolution. The only metastable visible in the spectra was at m/e 65.8 (m/e 140 → m/e 96). All the other metastable transitions were determined by the metastable defocusing technique.⁴ The primary processes found in the low voltage spectra and confirmed by high resolution and metastable defocusing are shown in Fig. 1.

An examination of the 70 eV spectra of the isomeric compounds, or those recorded at low voltage, showed that the spectra were very similar except for small intensity variations on different runs. Of interest in this discussion are the fragments m/e 64 and m/e 76. The fragment m/e 64, $C_6H_4^+$, is present in the spectra of both compounds and is in both isomers found to originate from the molecular ion by the loss of CS_2 . The fragment m/e 76 in both isomers was found to be a doublet containing CS_2^+ and $C_6H_4^+$ in the approximate ratio of 5:1. By lowering the energy of the electron beam to about 18 eV, only CS_2^+ was present, with no reduction in the intensity. In thieno[3,2-*b*]thiophene metastable defocusing on CS_2^+ showed transitions from m/e 102 [$M - C_3H_2$] and the molecular ion (m/e 140), the latter of very low intensity. In thieno[2,3-*b*]thiophene the transition from m/e 102 was absent, while the metastable from m/e 140 was of about twice the intensity of that observed for the other isomer.

The reduction of the intensity of m/e 76 in the low voltage spectra is surprisingly small compared with the other fragments,

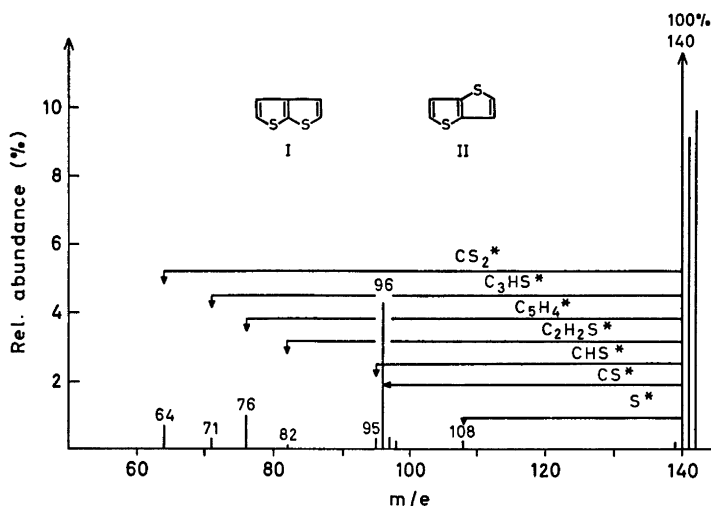


Fig. 1. Low voltage spectrum and primary fragmentation pattern for the thienothiophenes.

indicating that CS_2 may also be formed through thermal decomposition. In order to verify this assumption the nominal ionisation potentials of CS_2 from the compounds were compared with that of authentic CS_2 . Under the same source conditions the ionising voltage read 11.0 V when the intensity of the ion beam was 1% of the value at 50 eV. This value could be reproduced for both isomers and for the authentic CS_2 sample. This shows that CS_2 from the thienothiophenes has the same ionisation potential as authentic CS_2 . Contribution to CS_2^+ through pyrolysis is therefore possible.

It is evident from what is found for the fragments m/e 64 and m/e 76 that a skeletal rearrangement in thieno[3,2-b]thiophene at least, must have taken place prior to the fragmentation. Thiophenes and benzo[b]thiophene show similar skeletal rearrangements, found by Wynberg⁵ upon UV-irradiation and by de Jong¹ and Cooks² under electron impact, and are explained^{1,5} by suggesting the thiophenes to exist in a "Ladenburg" structure in the excited state.

The fragment m/e 102 [$\text{M} - \text{C}_3\text{H}_2$] is observed in the spectrum of thieno[3,2-b]thiophene with a relative abundance of about 0.1%. In the spectrum of thieno[2,3-b]thiophene this fragment is of even less abundance, if present at all. As previously mentioned the metastable transition m/e 102 \rightarrow m/e 76 (CS_2^+) is not ob-

served in the spectrum of thieno[2,3-b]thiophene. The metastable for the transition from the molecular ion (m/e 140) to CS_2^+ was also found to be of different intensity in the isomers. These small, but probably significant, differences between the thienothiophenes can be explained if one assumes that competition exists between direct fragmentation and isomerisation, but the latter seems to be by far the more important.

The ionisation potential measurements together with the relatively high abundance of CS_2^+ in the low voltage spectra may indicate that contribution to CS_2^+ comes from thermal processes. These are supposed to be due to the filament since no significant changes were observed in the spectra recorded with a source temperature of 50°.

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