# Analysis of Benzannelated Thiophene Derivatives by Negative-ion Chemical Ionization Using Oxygen as a Reagent Gas<sup>†</sup>

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Under the conditions of negative-ion chemical ionization with  $O_2$  as a reagent gas [NCI( $O_2$ )], thiophene derivatives suffer surface-catalysed oxidative degradation with subsequent ionization of the resulting species. These degradation reactions are to some extent structure specific and thus may be used for the localization of rings and/or substituents. It is advisable, however, to combine NCI( $O_2$ ) with either electron impact ionization or positive ion CI. The latter ionization methods yield abundant M<sup>++</sup> ions but hardly any structure-specific fragments, whereas with NCI( $O_2$ ) the determination of the molecular mass may be difficult owing to the competing oxidation reactions.

# INTRODUCTION

In one of the early publications on negative-ion chemical ionization (NCI) mass spectrometry, Hunt et al.<sup>2</sup> suggested that isobaric aromatic hydrocarbons and benzannelated thiophenes could be distinguished by their  $NCI(O_2)$  mass spectra: the former give M<sup>--</sup> and  $[M + 15]^{-}$  ( $[M + O - H]^{-}$ , phenolate) ions and the latter M<sup>-</sup> and  $[M + 32]^{-}$  ( $[M + 2O]^{-}$ , presumably sulphone)<sup>3</sup> ions. The importance of this observation for the analysis of high-boiling petroleum fractions was pointed out,<sup>2,3</sup> but only dibenzothiophene (1) was mentioned in the original publications,<sup>2,3</sup> and no further examples were added subsequently. In a preceding paper,<sup>1</sup> we showed that (i) gas-phase ionization of 1 occurs only to a minor extent, yielding  $[M + O - H]^{-1}$ ions (m/z 199), (ii) the bulk of the observed ions (see Table 1) arise from surface-catalysed oxidation and oxidative degradation processes as summarized in Scheme 1 (it should be noted that the ion at m/z 184 belongs to the degradation products and is not M<sup>--</sup> as had been assumed<sup>2,3</sup> by Hunt et al.) and (iii) that the ion at m/z216 ( $[M + 2O]^{-1}$ ), the most abundant ion in the upper mass range, actually is the sulphone anion. Since both electron impact (EI) ionization and positive-ion CI(O<sub>2</sub>) lead to  $M^{+}$  (m/z 184) as the most abundant species, the combination of the two modes of operation may well be used for an identification.

In this paper, we report the results obtained with methyl and ethyl derivatives of 1 and with di-, tri- and tetracyclic benzannelated thiophenes and discuss the influences of structural variations on the appearance of their  $NCI(O_2)$  spectra.

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### EXPERIMENTAL

#### Instrumentation

The NCI(O<sub>2</sub>) mass spectra were measured with a Varian-MAT (Bremen, Germany) Model 212 instrument equipped with a modified EI/CI source and a glow discharge probe<sup>4</sup> (discharge current 0.025–0.080 mA, discharge voltage 0.8–1.1 kV, source temperature 80-130 °C, pressure inside the source 40–60 Pa). Pressures inside the ion source were measured with a measuring probe equipped with a thermocouple vacuum gauge. NCI(O<sub>2</sub>) spectra were recorded without the conversion dynode. Samples were introduced with a

Table 1. Most important ions in the NCI(O<sub>2</sub>) mass spectrum of dibenzothiophene (1) (taken from Ref. 1)

m/z	Elemental composition	Assignment
64	SO2	S05'
73	C2HO3	
80	SŌ <sub>3</sub>	S0 <u>-</u> ,.
96	SO	SO4.
113	C <sub>4</sub> HO <sub>4</sub>	H00CC=CC00-
152	C <sub>7</sub> H₄SO <sub>2</sub>	a-'
168	C <sub>7</sub> H <sub>4</sub> SO <sub>3</sub>	b-'
184	C <sub>7</sub> H <sub>4</sub> SO <sub>4</sub>	c-'
199	C12H2SO	[M + O - H] - (phenolate)
200	C <sub>12</sub> H <sub>a</sub> SO	[M + O]-* (sulphoxide)
214	C <sub>12</sub> H <sub>6</sub> SO <sub>2</sub>	[M + 20 - 2H] <sup>-*</sup> (quinone)
216	C <sub>12</sub> H <sub>8</sub> SO <sub>2</sub>	[M + 20] <sup>-•</sup> (sulphone)
232	C <sub>12</sub> H <sub>8</sub> SO <sub>3</sub>	[M + 30]-*
248	C <sub>12</sub> H <sub>B</sub> SO <sub>4</sub>	[M + 40]-'
280	C12H8S2O4	$[M + SO_4]^{-1}, [M + 2O + SO_2]^{-1}$

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**Scheme 1.** Oxidation reactions of dibenzothiophene (1) under  $NCI(O_2)$  conditions (arrows indicate that the ions observed in the  $NCI(O_2)$  mass spectrum of 1 are formed by ionization of the respective oxidation products) (taken from Ref. 1).

modified<sup>5</sup> direct insertion probe (IGT, Much, Germany). For gas chromatographic/EI (GC/EI) measurements (electron energy 70 eV, emission current 1 mA, pressure  $2 \times 10^{-3}$  Pa, temperature 140 °C), samples were introduced via a Varian Model 3700 gas chromatograph (SE-54 fused-silica column).

#### Materials

 $O_2$  used as the reagent gas was supplied by Messer-Griesheim (Düsseldorf, Germany) (purity  $\ge 99.998\%$ ).

Benzo[b]thiophene was purchased from Aldrich (Steinheim, Germany), benzo[b]thiophene 1,1-dioxide, 3-methylbenzo[b]thiophene, 5-methylbenzo[b]thiophene and benzo[b]naphtho[2,1-d]thiophene from Lancaster Synthesis (Morecambe, Lancashire, UK), 3,5dimethylbenzo[b]thiophene from Maybridge (Tintagel, Cornwall, UK) and benzo[b]naphtho[1,2-d]thiophene from Promochem (Wesel, Germany). These compounds were used without further purification.

1-Methyldibenzothiophene,<sup>6,7</sup> 2-methyldibenzothiophene,<sup>8</sup> 3-methyldibenzothiophene,<sup>6,7</sup> 4-methyldibenzothiophene,<sup>8</sup> 2-ethyldibenzothiophene,<sup>9</sup> 4-ethyldibenzothiophene,9 1,3-dimethyldibenzothiophene,<sup>6,7</sup> 2,8dimethyldibenzothiophene,10,11 benzo[b]naphtho naphtho[2,3-b]thiophene,13,14 [2,3-d]thiophene,<sup>7,12</sup> naphtho[1,2-b]thiophene,<sup>15</sup> naphtho[2,1-b]thiophene,<sup>16</sup> 2-methylbenzo[b]thiophene,17 2-ethylbenzo[b]thiop-2,3-dimethylbenzo[b]thiophene<sup>18</sup> hene,17 and alkylbenzo[b]thiophene 1,1-dioxides<sup>19</sup> were prepared by literature procedures.

2-Fluorodibenzothiophene was prepared as follows. 2-Aminodibenzothiophene<sup>20,21</sup> was diazotized<sup>22</sup> and the resulting diazonium chloride was converted into the diazonium borofluoride<sup>23</sup> and decomposed thermally by sublimation<sup>24</sup> (90 °C, 133 Pa), yielding 2-fluorodibenzothiophene (m.p. 71 °C).

All compounds were characterized by GC/EI and by their  ${}^{1}$ H and  ${}^{13}$ C NMR spectra.

# **RESULTS AND DISCUSSION**

## Alkyldibenzothiophenes

The following compounds were investigated: 1-methyl-(2) (cf. Fig. 7 in Ref. 1), 2-methyl- (3) (Fig. 1), 3-methyl-(4), 4-methyl- (5), 1,3-dimethyl- (6) 2,8-dimethyl- (7), 2ethyl- (8), 4-ethyl- (9) and 2-fluorodibenzothiophene (10) (Fig. 2).



The appearance of their  $NCI(O_2)$  spectra corresponds to that of 1; the various ions (cf. Scheme 1) show the appropriate mass shifts, which proves that the introduction of additional substituents does not influence the oxidation reactions to a major extent. Compounds which have the two benzene rings differently substituted (2-6, 8-10) give two series of the ions corresponding to  $a^{-}-c^{-}$ , viz. m/z 152, 168, 184 for the unsubstituted and m/z 166, 182, 198 for the methyl- (2–5), 180, 196, 212 for the dimethyl- (6) and ethyl- (8, 9) and 170, 186, 202 for the fluoro-substituted compound (10). For the alkyl derivatives the ions stemming from the unsubstituted ring are more abundant than those from the substituted ring, which can be explained by the +I effect of the alkyl groups destabilizing negative ions. Correspondingly, the F-containing ions (-I effect) are more abundant for 10.

Oxidation of the CH<sub>3</sub> to the CHO group ( $\rightarrow$  [M + O - 2H]<sup>-•</sup>), which has been observed for polycyclic hydrocarbons,<sup>25,26</sup> is hardly discernible (e.g. m/z 212 for







2-5). Similarly, the ions formed by replacement of an alkyl group by  $O^{-*}$  ( $\rightarrow [M - R + O]^{-}$ )<sup>27,28</sup> are of low abundance (m/z 199 for the monosubstituted compounds; slightly more abundant for ethyl than for methyl).

Comparison of the NCI(O<sub>2</sub>) spectra of the isomeric methyldibenzothiophenes 2-5 shows that the position of the substituent has only very little influence on the oxidative breakdown of the system and hence a localization is not possible. For disubstitued compounds it is possible, however, to determine whether both substituents are located in the same ring or not. Thus, 7 shows only one series of degradation products (m/z 166, 182, 198) whereas 6 yields two of them differing by 28 u (m/z152, 168, 184 and m/z 180, 196, 212). For the same reason, a distinction is possible between a dimethyl and an ethyl derivative, etc. Also, dibenzothiophenes can be distinguished from isomeric naphtho thiophenes (see below).

### Benzo [b] naphtho [d] thiophenes

The three compounds benzo[b]naphtho[2,1-d]- (11, Fig. 3), benzo[b]naphtho[2,3-d]- (12, Fig. 4) and benzo[b]naphtho[1,2-d]thiophene (13, Fig. 5) have an additional benzene ring annelated to one of the benzene rings of dibenzothiophene (1). The sulphone anion ([M + 2O]<sup>-•</sup>, m/z 266) is the most abundant ion only for 11 and 13 (the species [M + O, 3O and 4O]<sup>-•</sup> (cf. Table 1) are also present). The most abundant ion for 12 and of appreciable abundance also for 11 and 13 is the quinone anion ([M + 2O - 2H]<sup>-•</sup>, m/z 264). Quinones



are typical oxidation products of polycyclic aromatic hydrocarbons (PAHs) under NCI( $O_2/N_2$ ) conditions where especially one of the central rings is transformed into a quinone.<sup>25,26,29</sup> From 12 a *p*- and from 11 and 13 the less favoured<sup>30</sup> o-quinoid structures (e.g. *e*, see Scheme 2) can be formed. This is reflected in the lower abundance of the *m/z* 264 ion (note that these quinones can also be obtained by CrO<sub>3</sub> oxidation of the



**Figure 3.** NCI( $O_2$ ) mass spectrum of benzo[*b*]naphtho[2,1-*d*] thiophene (11).







**Figure 5.** NCI( $O_2$ ) mass spectrum of benzo[b]naphtho[1,2-d] thiophene (13).

benzo [b] naphtho [d] thiophenes).<sup>31,32</sup> S-Oxidation of the quinones and/or quinone formation starting from the sulphoxide ( $\rightarrow m/z$  250) and the sulphone (e.g. f,  $\rightarrow f^{-1}$ , m/z 266) leads to ions at m/z 280 and 296 (e.g.  $q^{-1}$ ; final oxidative ring opening of the thiophene double bond of the quinone sulphone g (cf. the formation of d from 1) leads to  $h (\rightarrow h^{-1}, m/z 328)$ , which is the precursor of further degradation products. An analogous series of reactions can be formulated for the corresponding quinone sulphoxide. The fact that oxidative degradation does not occur prior to S-oxidation and quinone formation explains why in the mass region below m/z 200 the ion patterns of the three isomers differ only slightly in their relative abundances irrespective of whether the sulphone (11, 13) or the quinone (12) product prevails. The ions  $a^{-}-c^{-}$  (m/z 152, 168, 184) comprising the benzene ring are present. Analogous species with the naphthalene system (m/z 202, 218, 234)





are essentially missing owing to its facile oxidation to give quinones. The ion at m/z 176 (C<sub>9</sub>H<sub>4</sub>O<sub>4</sub> by exact mass measurement) can be formulated as  $j^{-+}$ , and that at m/z 148 is ionized phthalic anhydride ( $i^{-+}$ ). Phthalic anhydride can also react with O<sup>-+</sup> to give the phenolate ( $[i + O - H]^-$ , m/z 163). The ions  $i^{-+}$ ,  $j^{-+}$  and m/z 163 can also be found in the NCI(O<sub>2</sub>) spectra of fluorene and fluorenone.<sup>29,33</sup> Phenolate formation from intact molecules ( $[M + O - H]^-$ , m/z 249) is pronounced only for 13. For m/z 113, see Table 1.

The three isomeric benzo[b]naphtho[d]thiophenes can readily be distinguished by their NCI(O<sub>2</sub>) spectra (see Table 2). A distinction should also be possible from the isomeric anthra- and phenanthro[b]thiophenes, which cannot give the ions  $a^{-}-c^{-}$  as their formation requires the presence of a benzene ring annelated to the thiophene ring.

## Naphtho [b] thiophenes

The compounds naphtho [2,3-b] thiophene (14, Fig. 6), naphtho [2,1-b] thiophene (15, Fig. 7) and naphtho [1,2-b] thiophene (16, Fig. 8) are isomers of dibenzothio-







Figure 7.  $NCI(O_2)$  mass spectrum of naphtho[2,1-b]thiophene (15).



Figure 8. NCI( $O_2$ ) mass spectrum of naphtho[1,2-*b*]thiophene (16).

Table 2. Assignment of the most important ions in the  $NCI(O_2)$  spectra of the benzo[b]naphtho[d] thiophenes 11-13 and relative abundances of the ions suitable for their distinction

m/z	Assignment	Relative abundance	
148	<i>i</i> -•		
152, 168, 184	a-*, b -*, c -*		
163	[ <i>i</i> + O – H] <sup>_</sup>		
176	<i>j</i> -•		
249	$[M + O - H]^-$ (phenolate)	<b>11</b> 15%; <b>12</b> 5%; <b>13</b> 75%	
250	[M + O] <sup></sup> (sulphoxide)		
264	[M + 2O - 2H] -* (quinone)	<b>11</b> 56%; <b>12</b> 100%; <b>13</b> 43%	
266	[M + 20] <sup>-*</sup> (sulphone)	<b>11</b> 100%; <b>12</b> 13%; <b>13</b> 100%	
280, 296, 312, 328	$[M + O_n - 2H]^{-1}$ (n = 3-6)		
282, 298, 314, 330	$[M + O_n]^{-*}$ (n = 3-6)		



phene (1). As described for 11-13, they can form quinones by oxidation of the central ring ([M + 2O])-2H]<sup>-•</sup>, m/z 214), again the p-quinone derived from 14 being more pronounced than the o-quinones from 15 and 16. Sulphoxide ( $[M + O]^{-1}$ , m/z 200) and sulphone  $([M + 20]^{-1}, m/z 216)$  formation is of secondary importance for all three compounds. This seems to be characteristic for compounds with a terminal thiophene ring (see also the next section): obviously only compounds containing sulphur as an S-bridge are prone to extensive S-oxidation, in analogy with the observation that the CH<sub>2</sub> group of fluorene but not that of indene is into C=0 transformed а group under  $NCI(O_2/N_2/CO_2)$  conditions.<sup>26</sup>

Oxidative degradation of the quinones as discussed in the previous section leads to the ions at m/z 148  $(i^-)$ , 163  $([i + O - H]^-)$  and 176  $(j^-)$ , while the ions  $a^- -c^-$  are missing since they require the presence of a benzene ring annelated to the thiophene ring. For m/z113, see Table 1. The phenolate ion at m/z 199  $([M + O - H]^-)$  is of medium (14) to high abundance (15, 16), again reflecting the less favoured o-quinone formation from 15 and 16. Formation of  $[M - H]^-$  (m/z183) is observed for all three compounds 14-16 but not for the isomeric 1, and may be attributed either to dissociative electron capture or more probably to proton abstraction by OH<sup>-</sup> from the free thiophenic double bonds of 14-16.

The formation of several ions in the lower mass region can be explained (Scheme 3; cf. Table 3) by an oxidative cleavage of the free thiophene double bond (k)



Scheme 3. Oxidation reactions of naphtho[1,2-b]thiophene (16) under NCI( $O_2$ ) conditions.

and subsequent loss of the thus formed aldehyde and S-formate groups (see also the next section): m/z 187 ( $[k - CHO]^{-}$ ), 158 ( $[k - 2CHO]^{-}$ ), 203 ( $[k + O - CHO]^{-}$ ) and 174 ( $[k + O - 2CHO]^{-}$ ).

The NCI(O<sub>2</sub>) spectra of 14-16 predictably differ from that of the isomeric 1; 14, owing to the pronounced quinone anion formation ( $[M + 2O - 2H]^{-1}$ , m/z 214), can readily be distinguished from 15 and 16. Furthermore, inspection of the NCI(O<sub>2</sub>) spectra of 14-16 reveals that in the order 14, 15, 16 the abundances of the quinone anions decrease and those of ions such as  $[M + 2O - CHO]^{-}$  (m/z 187), which result from oxidative cleavages of the free thiophene double bonds, increase. The abundances of these two ions and that of the phenolate ion  $[M + O - H]^{-}$  (m/z 199) (the base peak for 15 and 16) can, therefore, be used for a distinction of 14, 15 and 16 (see Table 3).

### Benzo [b] thiophene (17) and its alkyl derivatives

In addition to 17 (Fig. 9), its 2-methyl (18, Fig. 10), 3methyl (19, Fig. 11), 5-methyl (20), 2,3-dimethyl (21), 3,5dimethyl (22) and 2-ethyl derivatives (23) were investigated. For the recurring low-mass ions, see Table 1. In



the upper mass range of the NCI(O<sub>2</sub>) spectrum of 17, the phenolate ion  $[M + O - H]^-$  (m/z 149) and, with lower abundance,  $[M - H]^-$  (m/z 133) can be recognized whereas  $[M + 2O]^-$  (m/z 166) (the sulphone and/or the oxidative cleavage product  $o^-$ ; see below)

Table 3. Assignment of the most important ions in the  $NCI(O_2)$ spectra of the naphtho[b]thiophenes 14-16 and relative abundances of the ions suitable for their distinction

m/z	Assignment	Relative abundance	
148	<i>i~</i> •		
158	[M + 20 – 2CHO] - '		
163	[ <i>i</i> + O – H] <sup>_</sup>		
171	[M + 20 – CHS] <sup>–</sup>		
174	[M + 30 – 2CH0] <sup>-•</sup>		
176	<i>j</i> -*		
183	[M – H]-		
187	[M + 20 - CHO] -	14 11%; <b>15</b> 25%; 16 58%	
199	[M + O - H] - (phenolate)	14 29%; 15 100%; 16 100%	
200	[M + O]		
203	[M + 30 – CHO] –		
214	[M + 2O – 2H] <sup>-+</sup> (quinone)	14 100%; 15 50%; 16 27%	
216	[M + 20] <sup>-*</sup> (e.g. k <sup>-*</sup> )		





Figure 10. NCI( $O_2$ ) mass spectrum of 2-methylbenzo[b]thiophene (18).



Figure 11.  $NCI(O_2)$  mass spectrum of 3-methylbenzo[b]thiophene (19).

are of minor importance. In addition to the phenolate ions ( $[M + O - H]^-$ ),  $[M + O]^{-*}$  and  $[M + OH]^$ are observed with varying abundance. For the two compounds substituted in the 2-position only (18 and 23),  $[M + O]^{-*}$  gives rise to the base peak; for the 2,3dimethyl derivative 21 it is, however, of medium abundance and it is surpassed by  $[M + OH]^-$ . The genesis of the three species is probably due to competing gasphase ion-molecule reactions<sup>29,34,35</sup> (addition of O could be a surface-catalysed sulphoxide formation, but in this case one would expect an even more pronounced  $[M + 2O]^{-*}$ ; cf. 1). For the reasons governing their formation only speculations could be offered.

The ion at m/z 137 corresponds to  $[M + 2O - CHO]^-$  and is accompanied by an ion at m/z 153, i.e.  $[M + 3O - CHO]^-$ . All the upper mass range ions are shifted by 14 u in the spectrum of 20, but

in addition to  $[M + 2O - CHO]^-$  the ion  $[M + 2O - CH_3CO]^-$  (m/z 137) of much lower abundance can be observed. The  $[M + 2O - RCO]^-$  ions (R = H or alkyl) from 17-23 are assembled in Table 2 (the  $[M + 3O - RCO]^-$  ions are always of lower abundance or missing). Formation of the ion at m/z 137 from 17, 18 and 23 could be due to the sequence  $l^{-*} \rightarrow m^{-*} \rightarrow n^-$  ( $l^{+*}$  fragments in this way under EI conditions [Eqn (1)].<sup>36</sup> This is unlikely, however, since under NCI(CH<sub>4</sub>) conditions the benzothiophene 1,1dioxides hardly show any such fragments, and with O<sub>2</sub> as the reagent gas they still yield [M + 2O - RCO]<sup>-</sup> and [M + 3O - RCO]<sup>-</sup> ions with R always stemming from the 2-position.



It is more probable, therefore, that the first step (as in the case of  $16 \rightarrow k$  above) is oxidative cleavage giving o, which after ionization loses 'CHO  $(p^{-})$  or is further oxidized to give finally  $q^{-}$  (Scheme 4). This interpretation is corroborated by the observation that the main products of an ozonolysis of 17 are 2-mercaptobenzaldehyde and -benzoic acid.<sup>37</sup> It is important to note that the loss of the S-acyl group  $(o \rightarrow p^-)$ , CHO from C-2 unsubstituted compounds, CH<sub>3</sub>CO' from 18 and 21 and  $C_2H_5CO$  from 23) is always more pronounced than the loss of 'CHO (or CH<sub>3</sub>CO' for 19 and 22) stemming from C-3 or from unspecific cleavages of the benzene ring (CH<sub>3</sub>CO' from 20, Scheme 5) (see Table 4). Unlike EI, which requires prior derivatization to the sulphones,<sup>36</sup> NCI(O<sub>2</sub>) allows, therefore, the determination of substituents at the 2-position.

## CONCLUSIONS

For polycyclic thiophene derivatives with a central thiophene ring,  $[M + 2O]^{-*}$  (sulphone) and  $[M + 2O - 2H]^{-*}$  (quinone) ions are the most important species.









Table 4.	Masses and	relative	abundances	(%, in
	parentheses)	of the	[M + 20 -	RCO] <sup>-</sup>
	ions from the	henzolb	1 thionhenes	17-23

Compound	R—H	R−CH <sub>3</sub>	R⊷C <sub>z</sub> H₅
17	137 (59)	123 ()	
18	151 ()	137 (14)	
19	151 (53)	137 (42)	
20	151 (80)	137 (18)	
21	165 (10)	151 (62)	
22	165 (55)	151 (28)	
23	165 ()	151 ()	137 (17)

Quinones are preferentially formed when a central benzene ring is present (11-16, and here again p-quinoid structures are favoured over o-quinoid structures. Phenolate ions ( $[M + O - H]^{-}$ ) are of varying abundance. The importance of  $[M + 2O]^{-1}$  decreases when the thiophene ring is located in a terminal position (14-16) and becomes negligible for benzothiophenes (17-23). Therefore,  $[M + 20]^{-1}$  ions are not characteristic for thiophenic compounds in general and can not be used to distinguish them from isobaric aromatic hydrocarbons as had been suggested earlier.<sup>2</sup> Oxidative ring degradation gains in importance for compounds with a terminal thiophene ring. These degradation reactions will give information regarding the localization of benzene rings and to a certain extent also of alkyl substituents. In combination with EI or positive-ion CI (which for the compounds investigated give M<sup>+</sup> but hardly any structurally relevant fragment ions),38  $NCI(O_2)$  can be used with success for the analysis of benzannelated thiophenes and their alkyl derivatives.

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