PROTON MAGNETIC RESONANCE SPECTRA OF BENZO(b)THIOPHENE DERIVATIVES

Sayeed Saraf, Saleh Al-Mousawi, and Muhammad Akram Khan

Chemistry Department, Kuwait University, Kuwait

Abstract —— Proton magnetic resonance spectra of substituted benzo(b)thiophenes is reviewed.

The proton magnetic resonance spectra of many aromatic and heterocyclic compounds have been studied in detail[1]. However, most of the detailed investigation of bicyclic system has been restricted to a refined study of the spectra of the parent compound and a few of its simple derivatives such as naphthylpyridine[2], benzofuran[3], indole[4], indazole[5], indazoline[6] and azaindazoline.[7-8] The influence of substituent on the chemical shift of ring protons in benzenoid polynuclear and heteroaromatic system has been the subject of a large number of communications[11-16] during the last decade. The benzo(b)-thiophene system has been studied by a number of workers[9-16] in the hope that the knowledge of the n.m.r. parameters, especially the influence of substituents on the chemical shifts of the ring protons would be useful in assigning structures to new derivatives in the series and, secondly, data of this type might be expected to throw some light on the influence of substituents on the n.m.r. parameters in aromatic systems in general.

Takahashi et al.[15] and Elvidge et al.[10] were the first to measure the chemical shifts of the six protons from partial deuteration experiments. It was observed that chemical shifts of the 5- and the 6-hydrogens are almost the same. The difference in the chemical shifts of about 0.5 ppm between the 4- and 5- or between 6- and 7-hydrogens was attributed to the ring current effect similar to that of naphthalene.[17] On the other hand, the larger chemical shift of the 7-hydrogen as compared to the 4-hydrogen has been attributed to the magnetic anisotropy or to the electronic effect of the sulphur atom.[15]

Chapman et al.[18] and Caddy et al.[19] have studied the substituent effects on the n.m.r. parameters in the benzo(b)thiophene series. According to Chapman et al.[18] the AB pattern arising from H-2 and H-3 in benzo(b)thiophene was totally obscured by the H-5, H-6 band and this made it difficult to estimate the chemical shifts for H-2 or H-3. The downfield shift of the benzenoid protons by 0.07 ppm was also observed, when deuteriochloroform was used as a solvent. The chemical shifts for 5-substituted benzo-(b)thiophene, and the measured substituents chemical shifts relative to benzo(b)thiophene or 3-methyl-benzo(b)thiophenes are summarised in Table 1 & 2.

TABLE 1

Chemical Shifts for Benzo(b)thiophenes[a, c]

Substituents	H_2	H_3	H_4	H_6	H_7	Ref.
5-Me[b]	7.26	7.12	7.49	7.05	7.64	18
5-Et[b]	7.18	7.08	7.47	7.02	7.62	18
5-Pr^i [b]	7.22	7.11	7.53	7.08	7.64	18
5-Bu^t [b]	7.23	7.15	7.69	7.28	7.66	18
5-OH[b]	7.12	7.38	7.19	6.88	7.65	18
	7.40	7.15	7.21	6.91	7.67	19
5-Br	.3	7.13	7.85	7.33	7.61	18
	7.44	7.23	7.92	7.40	7.69	19
	5.93	5.74	6.45	5.94	6.21	56
5-MeSO$_2$O	7.53	7.31	7.73	7.25	7.86	18
3-Me, 5-F[b]	7.02		7.29	7.07	7.66	18
3-Me, 5-Cl[b]	6.95		7.54	7.18	7.59	18
3-Me, 5-Br[b]	6.99		7.76	7.31	7.64	18
3-Me, 5-I[b]	6.88		7.90	7.45	7.43	18
3-Me, 5-Et[b]	6.86		7.38	7.05	7.60	18
3-Me, 5-NH$_2$	6.88		6.79	6.57	7.47	18
3-Me, 5-AcNH	6.98		7.94	7.28	7.62	18
3-Me, 5-CF$_3$[b]	6.99		7.86	7.44	7.75	18
3-Me, 5-CN	7.20		7.79	7.51	7.89	18
3-Me, 5-COOH	7.16		8.51	8.08	7.90	18
3-Me, 5-NO$_2$	7.23		8.54	8.14	7.87	18
3-CH$_2$Cl, 5-MeSO$_2$	7.57		7.78	7.32	7.86	18
3-CH$_2$Ac, 5-Cl	7.27		7.56	7.23	7.67	18
3-CN, 5-Cl	8.14		7.92	7.42	7.80	18
3-CHO, 5-Cl	8.33		8.69	7.41	7.78	18
3-Ac, 5-Cl	8.19		8.69	7.25	7.63	18
3-Br, 5-NO$_2$	7.62		8.71	8.25	7.95	18
	7.68		8.77	8.30	8.02	19
3-COOEt[b]	8.15		8.76	7.33	7.79	18
2-COOEt		7.88				18
2-Ac, 5-Cl		7.81	7.82	7.30	7.76	18
2-COOEt, 5-F		8.20	7.56	7.26	7.84	18
2-COOEt, 5-Cl		7.91	7.79	7.35	7.72	18
2-COOEt, 5-Br		7.91	7.95	7.49	7.66	18
2-COOEt, 5-I		7.83	8.10	7.59	7.49	18
2-COOMe, 5-OMe		7.95	7.26	7.09	7.09	18
2, 3-DiMe[b]			7.38	7.17	7.62	18
2, 3-DiMe, 5-Cl			7.41	7.11	7.49	18
2, 3-DiMe, 5-Br[b]			7.56	7.22	7.43	18

Substituents	H_2	H_3	H_4	H_6	H_7	Others	Ref.
2, 3-DiCH$_2$Br, 5-Br			7.77	7.34	7.69		18
2, 3-DiCH$_2$Br, 5-Cl			7.93	7.49	7.63		18
2-COOEt, 3-Me, 5-CF$_3$			8.05	7.62	7.87		18
2-COOEt, 3-Me, 5-NO$_2$			8.66	8.26	7.87		18
2-COOMe, 5, 6-OCH$_2$O-		7.86	7.16		7.16		18
5-NH$_2$	7.35	7.12	7.07	6.74	7.61	NH$_2$, 3.62	19
5-OMe	7.43	7.25	7.28	6.99	7.73	OMe, 5.28	19
5-OCOMe	7.36	7.18	7.48	7.03	7.63	COMe, 2.23	19
5-D	7.43	7.33	7.82	7.34	7.88		15
5-Cl	7.44	7.22	7.75	7.27	7.73		19
5-CH$_2$OH	7.42	7.26	7.73	7.26	7.81	OH, 2.17 CH$_2$, 4.73	19
5-CH$_2$Cl	7.45	7.30	7.81	7.35	7.84	CH$_2$, 4.68	19
5-CN	7.59	7.38	8.10	7.52	7.93		19
5-NHCOMe	7.39	7.15	8.11	7.32	7.70	COMe, 2.12, NH, 8.56	.19
5-I	7.41	7.23	8.16	7.59	7.59		19
5-CHO	7.55	7.46	8.28	7.85	7.98	CHO, 10.07	19
5-COOMe	7.51	7.42	8.54	8.00	7.91	COOMe, 3.94	19
5-COOH	7.54	7.45	8.62	8.07	7.96		19
5-NO$_2$	7.65	7.49	8.71	8.18	7.98		19
4-Br, 5-NH$_2$	7.45	7.35		6.80	7.53	NH$_2$, 4.05	19
2-COOMe, 5-NH$_2$		7.84	7.08	6.87	7.59	NH$_2$, 3.61, COMe, 3.89	19
4, 6-DiBr, 5-OMe	7.50	7.42			8.00	OMe, 3.94	19
2-COOMe, 5-OCOMe		7.97	7.57	7.16	7.80	COMe, 2.32, OMe, 3.93	19
4-Br, 5-NHCOMe	7.50	7.40		7.75	8.20	COMe, 2.25	19
3-CH$_2$COOH, 6-OEt	7.13		7.53		7.60	H-5, 7.00, CH$_2$CO, 3.78, OH 11.45. Et:1.38, 4.05	19
2-COOMe, 5-NHCOMe		7.95	8.20	7.50	7.77	OMe, 3.97, COMe, 2.62 NH, 8.17	19
2,3-DiBr, 5-NO$_2$			8.66	8.80	7.90		19
2-COOMe, 5-NO$_2$		8.22	8.80	8.33	8.02	OMe, 4.02	19
2-CONMe$_2$, 5-NO$_2$			7.73	8.75	8.28	NMe$_2$, 3.27	19
3-OMe, 5-NO$_2$	6.48		8.67	8.18	7.83	OMe, 4.02	19
3-COOMe, 5-NO$_2$	7.67		8.62	8.25	7.93	COMe, 2.43	19

a. In deuteriochloroform, unless otherwise indicated

b. In carbon tetrachloride

c. Chemical shifts are expressed in δ (ppm)

TABLE 2

SUBSTITUENT EFFECT ON H_{ortho} IN 5-SUBSTITUTED BENZO(b)THIOPHENES

| Substituent induced chemical shifts ($\Delta\delta$) in ppm			
Compound	Substituent	H_4	H_6
1	Me	0.21	0.19
2	Et	0.25	0.22
3	Pr^i	0.17	0.16
4	Bu^t	0.01	-0.04
5	OH	0.59	0.43
6	Br	-0.15	-0.09
7	NH_2[a]	0.75	0.60
8	OMe	0.54	0.35
9	OCOMe[a]	0.34	0.31
10	D	0	0
11	OSO_2Me[a]	0.07	0.08
12	Cl	0.07	0.07
13	CH_2OH	0.09	0.08
14	CH_2Cl	0.01	-0.01
15	CN	-0.28	-0.18
16	NHCOMe[b]	-0.29	0.02
17	I	-0.34	-0.25
18	CHO	-0.46	-0.51
19	COMe	-0.72	-0.66
20	COOH[c]	-0.80	-0.73
21	NO_2	-0.89	-0.84
22	3-Me, 5-F	0.32	0.17
23	3-Me, 5-Cl	0.07	0.06
24	3-Me, 5-Br	-0.15	-0.07
25	3-Me, 5-I	-0.29	-0.21
26	3-Me, 5-Et	0.23	0.19
27	3-Me, 5-NH_2	0.90	0.77
28	3-Me, 5-AcNH	-0.25	0.66
29	3-Me, 5-CF_3	-0.25	-0.20
30	3-Me, 5-CN	-0.29	-0.17
31	3-Me, 5-COOH	-0.82	-0.74
32	3-Me, 5-NO_2	-0.85	-0.80

Positive values denote an upfield shift for compounds (1-21) with respect to the unsubstituted substance, and with respect to 3-methylbenzo(b)thiophene for compounds (22-23).

a. Values obtained by extrapolation to infinite dilution in carbon tetrachloride.

b. Values obtained by extrapolation to infinite dilution in deuteriochloroform.

c. Indirectly obtained values

The plot of the chemical shifts of the two ortho protons (H-4 and H-6) in 5-substituted benzo(b)-thiophenes against each other gave a straight line, the slope of which was not 45°, thereby infer-ring that H-4 is more susceptible than H-6 to substituent effects.[19] This is particularly evident when the 5-substituent has a strong mesomeric interaction with the ring in the ground state (+ M effect): Canonical structure I probably contributes more to the ground state than the higher energy structure II.[18]


$$X = OH, NH_2 \text{ or } F$$
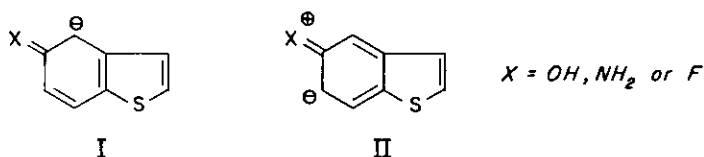
However, the consideration of the individual values (Table 2) shows that the effect is negligible for a number of cases where a substantial effect would be expected, is slightly reversed for the chloromethyl and formyl derivatives, but is significantly anomalous with the 5-acetamido derivative. This has been attributed to the higher relative population of the conformer (III) as compared to the conformer (IV).
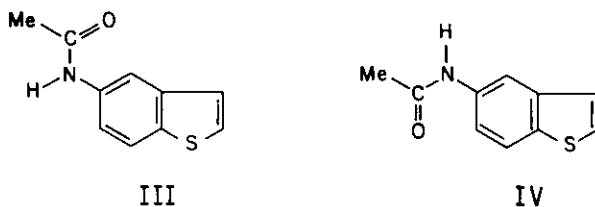

Measurement of the spectra over a range of temperature showed a significant change in the chemical shift of H-4 (by 0.10 ppm) to higher field with an increase of temperature, while the chemical shifts of H-7, H-2 and H-6 showed a slight change (0.02 - 0.03 ppm) over the same temperature range. This suggested that an imperfect averaging of long range shielding effects is involved.

The presence of an ethoxycarbonyl group in the 2-position produces a general deshielding of the ben-zene ring due to mesomeric effect. The deshielding is maximum at the 4- and 6-positions as expected from the mesomeric effect of the substituent (V).
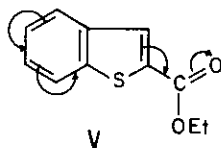
In case of 3-methylbenzo(b)thiophene, H-4 is clearly shielded relative to benzo(b)thiophene. In case of 4-methylbenzo(b)thiophene a reverse peri effect[9] plus shielding of H-3 has been observed. In contrast, a methyl substituent in systems containing two fused six membered rings deshields the peri position. A strongly anisotropic group such as COMe, COEt, CN and CHO in the 3-position causes a large deshielding of H-4 and allows the proton to be readily identified in the n.m.r. spectrum.[18]

The shielding of H-2 (ca. 0.40 Hz) by the methyl group in 3-methylbenzo(b)thiophene is much higher than the usual value for aromatic systems (ca. 0.17 Hz), thereby reflecting the high bond order of the 2, 3-bond.[18] A carbonyl group in the 3-position produces a downfield shift of H-2 which is larger than that of H-3 produced by a carbonyl group in the 2-position.[18, 80, 81] This suggests a greater contribution of structure VI relative to that of VII.
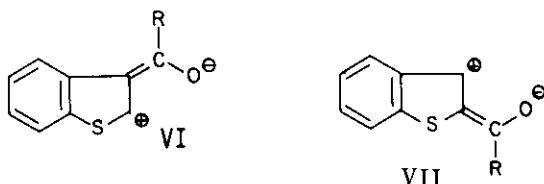
The ortho coupling constants ($J_{6, 7}$) for 5-substituted benzo(b)thiophene have values similar to the ortho coupling constants in benzene derivatives.[19. 18, 45, 82] The magnitude of J_{meta} coupling varies significantly with the nature of the substituent across the coupling path.[18, 19, 45, 82] No correlation with the electronegativity of the substituent has been observed. It can be seen from Table 3, that meta coupling across a substituent increases in the order: H < CF_3, CN, I < COOH, alkyl < Br, Cl, NO_2 < OH, OSO_2Me, NH_2 < F, OMe. This order is similar to the order of increasing $J_{6, 8}$ in the 7-substituted quinolines.[28]

TABLE 3

COUPLING CONSTANTS (C/S) FOR BENZO(b)THIOPHENES

Substituent	$J_{2, 3}$	$J_{6, 7}$	$J_{4, 7}$	$J_{3, 7}$	$J_{2, 6}$	$J_{4, 6}$	Ref.
5-Me	5.4	8.4	0.6	0.7	a	1.7	18
5-Et	5.4	8.5	b	0.6	a	1.8	18
5-Pr^i	5.5	8.4	b	0.6	a	1.7	18
5-Bu^t	5.6	8.3	0.6	0.7	a	1.7	18
5-NH$_2$	5.3	8.2	0.5	0.80	0.45	2.15	19
5-OMe	5.3	8.7	a	a	a	2.5	19
5-OCOMe	5.6	8.8	a	0.70	0.50	2.3	19
5-D	5.6	8.5	a	a	a	a	82

TABLE 3 (Contd.)

| Substituent	$J_{2,3}$	$J_{6,7}$	$J_{4,7}$	$J_{3,7}$	$J_{2,6}$	$J_{4,6}$	Ref.
5-OSO$_2$Me	5.3	8.4	a	a	a	2.4	19
5-Cl	5.60	8.6	0.5	0.75	0.50	2.0	19
5-CH$_2$OH	5.6	8.0	0.6	0.75	0.45	1.7	19
5-CH$_2$Cl	5.4	8.5	a	a	a	1.8	19
5-CN	5.6	8.2	0.6	0.70	0.50	1.6	19
5-NHCOMe	5.6	8.7	0.7	0.70	a	2.0	19
5-I	5.5	c	a	a	a	c	19
5-CHO	5.4	8.5	0.75	0.65	0.35	1.5	19
5-COOMe	5.3	8.4	a	0.70	a	1.4	19
5-COOH	5.6	8.4	a	a	a	1.5	19
5-NO$_2$	5.6	8.9	a	a	0.30	2.10	19
5-OH	5.5	8.5	0.6	0.7	b	2.3	18
5-Br	5.4	8.4	0.6	0.8	0.6	2.0	18
5-MeSO$_2$O	5.5	8.8	0.6	0.7	0.6	2.3	18
3-COOEt		8.2	0.6			1.2	18
2-COOEt		f	f	0.6		f	18
2-Ac, 5-Cl		8.5	0.6	0.6		2.0	18
2-COOEt, 5-F[h]		8.6	d	0.6		2.5	18
2-COOEt, 5-Cl		8.4	0.6	0.7		2.1	18
2-COOEt, 5-Br		8.5	0.5	0.7		1.9	18
2-COOMe, 5-OMe		8.8	0.6	0.7		2.5	18
2, 3-DiMe, 5-Cl		8.3	0.4			2.3	18
2, 3-DiMe, 5-Br		8.5	0.6			1.8	18
2, 3-DiCH$_2$Br, 5-Cl		8.5	0.7			2.0	18
2, 3-DiCH$_2$Br, 5-Br		8.5	0.6			2.0	18
2-COOEt, 3-Me, 5-CF$_3$		8.4	0.6			1.4	18
2-COOEt, 3-Me, 5-NO$_2$		8.7	0.6			2.0	18
2-COOMe, 5,6-OCH$_2$O			0.6	0.6			18
4-Br, 5-NH$_2$	5.7	8.9		0.7	0.4		19
2-COOMe, 5-NH$_2$		8.8	0.60	0.60		2.4	19
4, 6-DiBr, 5-OMe	5.6			0.60			19
2-COOMe, 5-COOMe		8.6	0.60	0.8		2.3	19
4-Br, 5-NHCOMe	5.5	9.0					19
2-COOMe, 5-NHCOMe		8.9				2.0	19
2, 3-DiBr, 5-NO$_2$		8.9				2.3	19
2-COOMe, 5-NO$_2$		9.1	0.5	0.9		2.3	19
2-CONMe$_2$, 5-NO$_2$		9.0	0.5	0.8		2.0	19
3-OMe, 5-NO$_2$		8.8	0.65		0.5	2.2	19
3-COOMe, 5-NO$_2$	$J_{2,3'}$	9.2	0.6			2.2	19
3-Me, 5-F[d]	1.1	8.5	b		a	2.5	18
3-Me, 5-Cl	1.2	8.3	0.6		0.6	2.1	18
3-Me, 5-Br	1.1	8.6	0.6		0.5	1.8	18

TABLE 3 (Contd.)

Substituents	$J_{2, 3}$	$J_{6, 7}$	$J_{4, 7}$	$J_{3, 7}$	$J_{2, 6}$	$J_{4, 6}$	Ref.
3-Me, 5-I	1.1	8.8	0.6		a	1.4	18
3-Me, 5-Et	1.2	8.2	0.7		a	1.7	18
3-Me, 5-NH$_2$	a	8.5	0.6		0.6	2.2	18
3-Me, 5-AcNH	b	8.7	b		b	b	18
3-Me, 5-CF$_3$	1.1	8.4	0.6		b	1.4	18
3-Me, 5-CN	1.2	8.5	0.7		a	1.5	18
3-Me, 5-COOH	1.1	8.6	0.6		a	1.7	18
3-Me, 5-NO$_6$	1.1	8.7	0.6		0.6	2.1	18
3-CH$_2$Cl, 5-OSO$_2$Me	1.1	8.5	0.6		0.6	2.3	18
3-CH$_2$Ac, 5-Cl	1.1	8.8	0.6		b	2.1	18
3-CN, 5-Cl	1.1	8.7	0.6		0.5	2.2	18
3-CHO, 5-Cl		8.5	0.6		0.5	2.0	18
3-Ac, 5-Cl		8.5	0.6		c	2.0	18
3-Br, 5-NO$_2$		8.5	0.6		0.6	2.0	18

a. Less than the resolution of the instrument.   b. This parameter could not be extracted from a complex spectrum.   c. Not measured.   d. $J_{4, F}$ 9.4; $J_{6, F}$ 9.0; $J_{7, F}$ 4.8 c/sec. $J_{4, 5}$ 8.2; $J_{5, 6}$ 7.0; $J_{5, 7}$ 1.2 c/sec.   h. $J_{4, F}$ 8.6; $J_{6, F}$ 6.0 c/sec.

$J_{2, 3}$ (ca 5.5 Hz)[9, 12, 15, 82-86] is smaller than the benzenoid ortho coupling constant and is not markedly affected by substituents in the benzene ring.[18, 19] The well established long-range coupling between H-3 and H-7 ($J_{3, 7}$ = 0.6 - 0.8 Hz)[16, 45, 83-86] and H-2 and H-6 ($H_{2, 6}$ = 0.5 - 0.6 Hz)[45, 84, 85, 86] in benzo(b)thiophene derivatives is believed to take place along the "straight Zig-Zag" (trans) conjugated pathways (VIII) and (XI).[85, 87, 88] Smaller long-range coupling (< 0.3 Hz)[19] is sometimes observed between H-3 and H-4 and possibly between H-2 and H-4.[16, 18] Although H-2 and H-5 are connected

VIII   IX
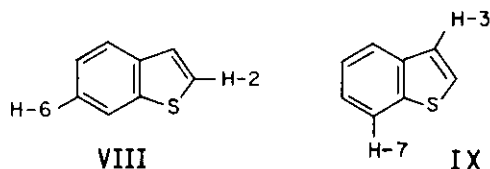
by a straight "Zig-Zag" pathway, long-range coupling between them has not been observed.[16]

In case of 3-methylbenzo(b)thiophene and 3-methyl-5-ethylbenzo(b)thiophene, a fairly well resolved multiplet for H-4 consistent with $J_{4, 6}$ = 1.7, $J_{4, 7}$ ≈ $J_{4, 5}$ = 0.6 c/sec. is observed. Benzo(b)thiophenes containing a methyl substituent in the benzene ring show coupling of the methyl protons (ortho side-chain coupling, J = 0.6-0.7 Hz)[12, 81] and a much smaller coupling with other ring protons.[12] Much larger splitting are observed between H-3 and a 2-methyl group ($J_{2, 3}$ ≈ 1.1-1.5 Hz[12, 14, 19]) owing to the more localized nature of the 2, 3-doubled bond. A similar effect is observed in the case of mercaptobenzo(b)thiophene ring.[45] In case of 3-methyl-5-trifluoromethylbenzo(b)thiophene, substantial coupling between CF_3 and with H-7 (J_7, CF_3 = 0.7 Hz) and also with the adjacent ring proton (J_4, CF_3 = 0.7),[18] was observed. 2, 3-Dimethyl-benzo(b)thiophene shows homobenzylic coupling ($J_{2, 3}$ = 0.75 or 0.8 Hz).

N.m.r. spectroscopy has been successfully utlized in the structural determination of various substituted benzo(b)thiophenes. The method has been found of particular value in case of nitrobenzo(b)thiophenes, in which the long-range coupling constants are readily measured.[45]

The mixture resulting from the reaction of nitric acid in acetic acid with benzo(b)thiophene at 60°C was analysed quantitatively by n.m.r. spectroscopy. The results indicated the complete absence of the 5-nitro isomer and gave the approximate proportion of 3, 4, 2, 7, and 6-nitrobenzo(b)thiophenes present as 56:13:12:11:10.[42]

Substitution of the nitro group into the benzene ring of the heterocyclic molecule yielded an easily resolved ABX spectrum with a superimposed long-range 2, 6 and/or 3, 7-coupling of 0.3 to 0.9 cps. This long-range coupling between the 2, 6-protons and between 3, 7-protons in benzo(b)thiophene is known to occur.[43, 44] The unsymmetrical 2- and 3-nitrobenzo(b)thiophenes has an ABXY pattern, but was difficult to analyse due to long-range couplings. However, the long-range 2, 6 and 3, 7-coupling facilitated the analysis since it allowed the pinpointing of the 6- and 7-protons.[45] Coupling constants $J_{4, 5}$ and $J_{6, 7}$ are larger than $J_{5, 6}$ which must be due to partial bond fixation.

Analysis of the chemical shifts in the isomeric mononitrobenzo(b)thiophenes in terms of down field shifts with respect to the signals from the corresponding protons in benzo(b)thiophene itself reveals that an ortho-relationship to the nitro group gives a shift of 0.81-1.19 ppm, a meta-relationship gives a shift of 0.9-0.19 ppm, and a peri-relationship gives a shift of 0.72-0.88 ppm. The largest downfield shifts caused by the nitro group at more remote positions are those for 2-H and 4-nitrobenzo(b)thiophene and 6-nitrobenzo(b)thiophene.

In case of 3, X-dinitrobenzo(b)thiophene (X), the spectra can be regarded as arising from 3-spin system due to protons on the benzene ring, with cross ring coupling due to 2-H as a first order perturbation. The relative magnitude of J_o, J_m and J_p permitted instant identification of (Xa) and Xd)

X

Xa, X=7-NO₂ ... Xb, X=6-NO₂
Xc, X=5-NO₂ ... Xd, X=4-NO₂
Xe, X=4,6 (NO₂)₂
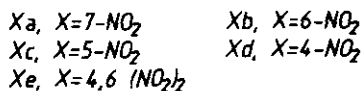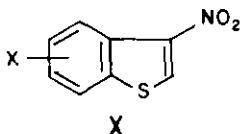
as 1, 2, 3-trisubstituted benzenes ' and of (Xb) and (Xc) as 1, 2, 4-trisubstituted ' benzenes. The established coupling between 2-H and 6-H permitted ready distinction between structures (Xa) and (Xb), while the extreme downfield shift of 4-H in (Xc) ascribable to a combination of ortho to nitro and peri effects, further distinguishes compounds (Xb) and (Xc). Higher chemical shift in (Xd) as compared to (Xb) was attributed to both magnetic anisotropy of the nitro group[48] and the steric suppression of ground state mesomeric effects.[42]

Nitration of 2-bromo-3-methylbenzo(b)thiophene gave a mixture of products from which 2-bromo-3-methyl-4-nitrobenzo(b)thiophene was identified by its n.m.r. spectrum. Its benzenoid protons showed the coupling pattern expected for either a 4- or 7-nitro derivatives. The signals due to the proton ortho or para to the nitro group were exerting their full mesomeric effect which is expected from 4-nitrobenzo(b)thiophene.[46]

The other product 3-methyl-3-nitrobenzo(b)thiophene-2(3H)-one (XI) showed the presence of 4 benzenoid

XI
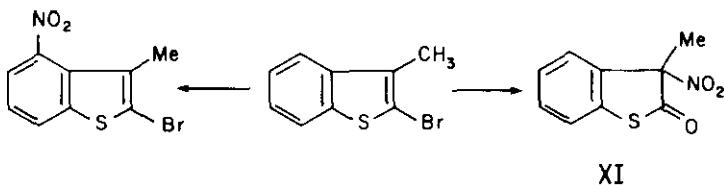
protons and a tertiary methyl group (δ 2.03 ppm). Despite the presence of an adjacent nitro group the latter signal appears at higher field than the methyl signal for 2-bromo-3-methylbenzo(b)thiophene (δ 2.32 ppm), thus suggesting the loss of thiophene ring current during the formation of XI in the nitration reaction.

TABLE 4

Chemical shifts δ (ppm) and coupling constants J (Hz) for the nitrobenzo(b)thiophene protons[a]

Substituent	H-2	H-3	H-4	H-5	H-6	H-7	Others	Coupling Constants (Hz)	Ref.
2-NO$_2$		8.18	7.88	7.46	7.54	7.79		$J_{3,7}$ 0.77; $J_{4,5}$ 8.49; $J_{4,6}$ 1.13; $J_{4,7}$ 0.82; $J_{5,6}$ 7.21; $J_{5,7}$ 1.05; $J_{6,7}$ 8.31;	42
		7.87	7.63	7.22	7.12	7.50		$J_{3,7}$ 0.38;	45
3-NO$_2$	8.62	-	8.53	7.54	7.46	7.82		$J_{2,6}$ 0.36; $J_{4,5}$ 8.47; $J_{4,6}$ 1.15; $J_{4,7}$ 0.71; $J_{5,6}$ 7.24; $J_{5,7}$ 1.06; $J_{6,7}$ 8.33;	42
4-NO$_2$	8.47	8.21	-	8.33	7.45	8.16		$J_{2,3}$ 5.80; $J_{2,6}$ 0.50; $J_{3,7}$ 0.90; $J_{5,6}$ 8.0; $J_{6,7}$ 8.20; $J_{5,7}$ 1.0	42
	7.76	8.03	-	8.01	6.81	7.48		$J_{5,6}$ 8.07; $J_{5,7}$ 0.86; $J_{6,7}$ 8.03	45
5-NO$_2$	7.14	7.48	8.70	-	8.19	7.97		$J_{2,3}$ 5.6 ; $J_{6,7}$ 8.9 ; $J_{4,6}$ 2.1; $J_{4,7}$ 0.6; $J_{3,7}$ 0.7; $J_{2,6}$ 0.3	42
	7.67	7.69	8.31	-	7.45	7.19		$J_{2,3}$ 2.55; $J_{2,6}$ 0.15; $J_{3,7}$ 0.20; $J_{4,6}$ 1.71; $J_{4,7}$ 1.30; $J_{6,7}$ 6.33;	45
6-NO$_2$	7.80	7.45	7.91	8.22	-	8.80		$J_{2,3}$ 5.5 ; $J_{4,5}$ 8.9 ; $J_{5,7}$ 2.1; $J_{4,7}$ 0.5 ; $J_{3,7}$ 0.8	42
	7.24	6.94	7.34	7.95	-	8.37		$J_{2,3}$ 5.5 ; $J_{3,7}$ 0.74; $J_{4,5}$ 9.07; $J_{4,7}$ 0.62; $J_{5,7}$ 2.16;	45
7-NO$_2$	7.66	7.48	8.14	7.53	7.40	-		$J_{2,3}$ 5.5 ; $J_{4,5}$ 8.0 ; $J_{5,6}$ 8.0; $J_{4,6}$ 1.0 ; $J_{2,6}$ 0.5	42

TABLE 4 (Contd.)

Chemical shifts δ (ppm) and coupling constants J(Hz) for the nitrobenzo(b)thiophene protons[a]

Substituent	H-2	H-3	H-4	H-5	H-6	H-7	Others	Coupling Constants (Hz)	Ref.
7-NO$_2$	7.49	6.64	7.33	7.07	7.22	-		$J_{2,3}$ 2.20; $J_{2,6}$ 0.45; $J_{4,5}$ 7.97; $J_{4,6}$ 1.08; $J_{5,6}$ 7.83;	45
2,3-Br$_2$, 5-Me, 4-NO$_2$[c]	-	-	-	-	7.29	7.72	2.40		47
2,3-Br$_2$, 5-Me, 6-NO$_2$	-	-	7.66	-	-	8.43	2.73		47
2,3-Br$_2$, 4-NO$_2$[c,d]	-	-	-	7.59	7.43	7.87	-		47
2,3-Br$_2$, 6-NO$_2$[c]	-	-	7.82	8.27	-	8.64	-		47
4-NO$_2$	8.17	-	-	8.59	7.80	8.24	-		47
2-Br, 3-CH$_3$, 4-NO$_2$	-	-	-	7.63(dd)	7.37(dd)	7.88(dd)	2.28(S,Me)	$J_{5,6}$ 8.2; $J_{5,7}$ 1.2; $J_{6,7}$ 7.9;	45
2-Br, 3-Me, 6-NO$_2$	-	-	7.70(dd)	8.21(dd)	-	8.62(dd)	2.42(S,Me)	$J_{4,5}$ 8.7; $J_{5,7}$ 2.3; $J_{4,7}$ 0.6;	46
2-COOEt, 3-Me, 4-NO$_2$, 5-OCH$_3$	-	-	-	-	8.18(d)	7.9(d)	2.23(S,Ac) 2.55(S,Ar-Me) 8.01 br(NH)		46

a = CDCl$_3$

b = (CD$_3$)$_2$CO

c = Analysed as ABX and/or AB

Bromination of 5-amino-3-methylbenzo(b)thiophene gave 5-amino-4-bromo-3-methylbenzo(b)thiophene.[33] Its structure was established by n.m.r. spectrum which showed clearly the 6- and 7-proton signals as ortho-coupled doublets $J_{6,7}$ = 8.3 c/sec, with the peaks due to 6-proton further split by long range coupling with the 2-proton ($J_{2,6}$ = 0.6 c/sec).

N.m.r. spectrum of 7-substituted 4-methoxybenzo(b)thiophene showed two distinct AB quartets due to 5-H, 6-H, 2-H and 3-H, which were easy to distinguish due to the higher value of the coupling between two adjacent benzenoid protons ($J_{5,6}$ = 8Hz) as compared to the two adjacent thiophene protons ($J_{2,3}$ = 5.7 Hz).[34] Long-range coupling[18] (ca. 0.5 Hz) between 2-H and 6-H enabled the assignment of the signals due to 2-H and 6-H. The absence of such coupling in the spectra of 2, 7-dibromo- or 2, 7-dinitrobenzo(b)thiophenes confirmed the presence of a 2-substituent. Due to the presence of 4-methoxy group, the 3-H signal appeared at lower field than the 2-H signal. The 5-proton was strongly shielded by the 4-methoxy group, which helped in its assignment.

Synthesis of the sulphur analog of psilocin (XII) carried out by two different research groups has been reported,[35, 36] but with different physical constants of some of the common intermediates. The
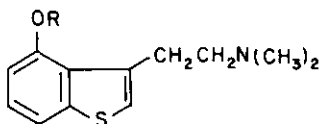
XII

XIIa, R=H   *XIIb, R=CH₃*

structures of various intermediates involved in the synthesis was finally established by n.m.r. spectroscopy. The main intermediate, 4-methoxy-3-methylbenzo(b)thiophene gave a multiplet at δ 6.76 (2-H), doublet of doublet at δ 6.50 (5-H), quartet at δ 7.16 (6-H), doublet of doublet at δ 7.32 (7-H), singlet at δ 3.79 (4-OCH₃) and doublet at δ 2.56 (3-CH₃).[36] These values differed from those of Chapman et al.[35], who had reported a quartet at δ 6.80 (2-H), singlet at δ 3.85 (4-OCH₃) and a doublet at δ 2.60 (3-CH₃). These data showed that the methyl group is either attached to C-2 or C-3 and coupled to either H-3 or H-2.

Different coupling constants ($J_{2,3}$' = 1.1 - 1.5[37], 1.1 - 1.5[38], 0.08[35, 39], 1.1 - 1.4[36] Hz) between a proton at C-2 and a methyl group at C-3 have been reported. This confused reporting of coupling constants was solved by the synthesis of 4-methoxy-2-methylbenzo(b)thiophene, in which the coupling constant between a proton at C-3 and a methyl group at C-2 was found equal to 1.0.[65]

Further treating the compound XIIb with butyl lithium and quenching the resulting lithiobenzo(b)thio-phene with deuterium oxide resulted in the formation of XIIb deuterated at C-2, the n.m.r. spectrum

of which showed the complete disappearance of the signal at δ 6.92 with the remainder of the spectrum being unchanged.

Iddon and Scrowston[40] have reported that cyclisation of ketosulphides with polyphosphoric acid may result in rearrangement to produce 2-substituted benzo(b)thiophenes. However, this was shown not to occur in the cyclisation of 3, 4-disubstituted phenylthioacetoacetates (XIV), which yielded a 3-substituted benzo(b)thiophene. This was confirmed by treating compound XV with butyl lithium followed


XIV, $R_1 = R_2 = CH_3$
$R_1 = H$; $R_2 = CH_3$
$R_1 = CH_3$; $R_2 = H$

NH_3/CH_3COOH

Red

XV
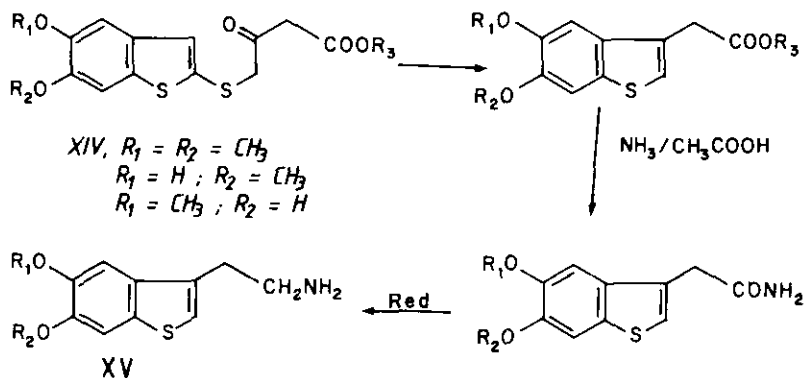
by deuterium oxide. The deuterated compound thus obtained exhibited only two signals at δ 7.2 and 6.95 as compared to the n.m.r. spectrum of XV, which exhibited three singlets for aromatic protons at δ 7.2, 6.95 and 6.8. The protons at position 2- and 3-alkylbenzo(b)thiophenes have been shown to occur in the range of δ 7.67 - 6.89.[65]

Cyclisation of XVI gave a quite satisfactory yield of the benzo(b)thiophene-2-carboxylic acid (XVII).[41] The acid and its methyl ester were characterised by their n.m.r. spectra, which exhibited characteristic singlets for protons at the 3-position at δ 8.12 ± 0.5 for a single proton adjacent to a methyl group at position-4 in the range of δ 7.73 ± 0.10 or at δ 7.41 ± 0.14 for a single proton

XVI

XVIIa, $R=CH_3$; $R_1=CH_3$; $R_2=OCH_3$
XVIIb, $R=H$; $R_1=OCH_3$; $R_2=CH_3$
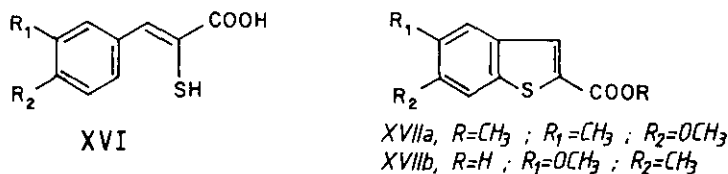
adjacent to a methoxy group. The singlet protons at position-7 are in approximately the same range, at δ 7.43 ± 0.18 when flanked by a methoxy group at 6 (XVIIa, XVIIb) and at δ 7.75 ± 0.08 when flanked
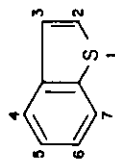
by a methyl group at 6 (XVIIIa or XVIIIb). These data are consistent with cyclisation occurring·

$$H_3CO \quad\quad S \quad COOR$$

$$H_3C$$

XVIIIa ; R=H
XVIIIb ; R=CH₃
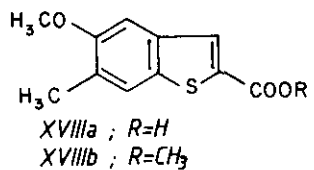
only to position para to methyl or methoxy groups respectively and the chemical shifts are in the

range as expected.

N.m.r. results are given in Tables 5, 6, 7 and 8.

TABLE 5

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment)	Ref.
2-CH$_3$ [k, b]	5.40(H-3), 6.10(H-4), 5.7(H-5), 5.7(H-6), 6.10(H-7), 1.09(CH$_3$)	19
3-CH$_3$ [k, b]	5.51(H-2), 6.2(H-4), 5.8(H-5), 5.8(H-6), 6.2(H-7), 0.96(CH$_3$)	19
4-CH$_3$ [k, b]	5.86(H-2), 5.59(H-5), 5.73(H-6), 6.16(H-7), 1.14(CH$_3$)	19
5-CH$_3$ [b]	5.83(H-2), 5.67(H-3), 6.04(H-4), 5.60(H-6), 6.20(H-7), 0.99(CH$_3$)	19
6-CH$_3$ [k, b]	5.78(H-2), 5.73(H-3), 6.16(H-4), 5.63(H-5), 6.14(H-7), 1.0 (CH$_3$)	19
7-CH$_3$ [k, b]	5.85(H-2), 5.60(H-3), 6.12(H-4), 5.76(H-5), 5.57(H-6), 1.10(CH$_3$)	19
3, 5-Br$_2$ [k, b]	5.97(H-2), 6.50(H-4), 6.03(H-6), 6.22(H-7)	56
3-COCH$_3$, 5-Br [k, b]	6.71(H-2), 5.97(H-6), 6.15(H-7), 1.10(CH$_3$)	56
2-COCH$_3$, 5-Br [k, b]	6.30(H-3), 6.52(H-4), 6.07(H-6), 6.26(H-7), 1.15(CH$_3$)	56
6-COOCH$_3$ [k, b]	6.13(H-2), 5.88(H-3), 6.35(H-4), 6.54(H-5), 7.13(H-7), 2.47(CH$_3$)	56
3-Br, 6-COOCH$_3$ [k, b]	6.12(H-2), 6.36(H-4), 6.59(H-5), 7.07(H-7), 2.49(CH$_3$)	56
2, 3, 5-Me$_3$ [b]	7.33(H-4), 7.05(H-6), 7.55(H-7), 2.44(2, 3-Me$_2$), 2.24(5-Me)	55
2-CHO [b]	7.95(H-3), 7.7-7.95(4, 7-H), 7.3-7.55(5, 6-H), 10.02(CHO)	55
5-Cl, 2-CHO [b]	7.94(H-3), 7.89(H-4), 7.43(H-6), 7.80(H-7), 10.10(CHO)	55
3-Br, 6-COCH$_3$ [b]	6.12(H-2), 6.36(H-4), 6.50(H-5), 6.94(H-7), 1.17(CH$_3$)	56
4-Br, 3-CH$_3$ [b]	6.92(m, 2-H), 7.41(dd, 5-H), 6.95(dd, 6-H), 7.60(dd, 7-H), 2.63(br, s, Me), (J$_{6, 7}$ 8.0, J$_{5, 6}$ 7.5, J$_{5, 7}$ 1.0, J$_{2, 6}$ 0.6)	65
2, 5-(CH$_3$)$_2$ [b]	6.78(q, H-3), 7.35(d, H-4), 7.53(d, H-7, J 8.5), 6.99(dd, H-6), 2.53(d, 2-CH$_3$, J 1.2), 2.41(5-CH$_3$)	66

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment	Ref.
5-Cl, 2-CH$_3$	6.90(q, H-3), 7.65(d, H-4), J 1.8), 7.65(d, H-7, J 8.7), 7.22(dd, H-6), 2.57(d, 2-CH$_3$, J 1.2)	66
2-SCH$_3$	7.04(H-3), 7.70-7.40(m, H-4 and H-7), 7.30-7.70(m, H-5 and H-6), 2.42(SCH$_3$)	66
5-CH$_3$, 2-SCH$_3$	7.03(H-3), 7.30(d, H-4, J 2.0), 7.49(d, H-7, J 8.0, 6.97(dd, H-6), 2.48(SCH$_3$), 2.38(CH$_3$)	66
5-Cl. 2-SCH$_3$	6.97(H-3), 7.50(d, H-4, J 2.2), 7.52(d, H-7, J 8.5), 7.15(dd, H-6), 2.53(SCH$_3$)	66
2, 5-Me$_2$, 3-Br	7.52(d, H-4), 7.15(dd, H-6), 7.58(H-7), 2.50(CH$_3$), 2.47(CH$_3$), (J$_{4,6}$ 1.7, J$_{6,7}$ 8.2)	66
2-Me, 3-Br, 5-Cl^b	7.69(d, H-4), 7.22(dd, H-6), 7.53(d, H-7), 2.53(CH$_3$), (J$_{4,6}$ 2.0, J$_{6,7}$ 8.2),	66
	7.63-6.90(4, 5, 6 and H-7), 2.35 (CH$_3$)	
2-SCH$_3$, 3-Br, 5-CH$_3$	7.51(dd, H-4), 7.56(d, H-7), 2.53(SCH$_3$), 2.45(5-CH$_3$), (J$_{4,5}$ 1.7, J$_{6,7}$ 8.2)	66
2-SCH$_3$, 3-Br, 5-Cl^b	7.54(d, H-4), 7.15(dd, H-6), 7.44(d, H-7), 2.53(SCH$_3$), (J$_{4,6}$ 2.0, J$_{6,7}$ 8.2)	66
2-CH$_3$, 3-CHO^b	8.47(H-4), 7.50-7.20(s and H-6), 7.64(H-7), -0.18(CHO), 2.75(CH$_3$), 2.56(5-CH$_3$), (J$_{4,6}$ 1.8, J$_{6,7}$ 8.0)	66
2-CH$_3$, 5-Cl, 3-CHO	8.62(d, H-4), 7.30(dd, H-6), 7.62(d, H-7), 0.28(CHO), 2.88(CH$_3$), (J$_{4,6}$ 2.0, J$_{6,7}$ 8.5)	66
2-SCH$_3$, 3-CHO^b	8.47(m, H-4), 7.50-7.30(5 and H-6), 7.63(H-7), -0.32(CHO), 2.66(SCH$_3$)	66
2-SCH$_3$, 5-CH$_3$, 3-CHO	8.25(d, H-6), 7.18(dd, H-6), 7.61(d, H-7), -0.42(CHO), 2.67(SCH$_3$), 2.48(5-CH$_3$) (J$_{4,6}$ 1.8, J$_{6,7}$ 8.0)	66
2-SCH$_3$, 5-Cl, 3-CHO	8.41(d, H-4), 7.27(dd, H-6), 7.58(d, H-7), -0.04(CHO), 2.80(SCH$_3$), (J$_{4,6}$ 2.0, J$_{6,7}$ 8.5)	66
4-OH, 5-Br^d	7.42(2-H), 7.42(3-H), 7.65(6-H), 7.65(7-H), 8.45(OH)	67
5, 7-Br$_2$, 4-OH	7.42(d, H-2), 7.55(d, 3-H), 7.47(6-H), 5.80(OH), (J$_{2,3}$ 5.96, J$_{2,6}$ 0.5)	67
4-OH, 5-NO$_2$	7.42(d, H-2), 7.72(d, 3-H), 8.02(d, 6-H), 7.42(d, 7-H), 11.51(OH), (J$_{2,3}$ 5.5, J$_{5,6}$ 8.35, J$_{2,6}$ 0.5)	67
4-OH, 7-NO$_2$	7.65(d, H-2), 7.75(d, 3-H), 7.03(d, 5-H), 8.31(d, 6-H), 8.80(OH), (J$_{2,3}$ 5.95, J$_{5,6}$ 8.35, J$_{2,6}$ 0.5)	67
5,7-(NO$_2$)$_2$^{d}	7.35(d, H-2), 7.55(d, 3-H), 7.75(6-H), 8.95(OH), (J$_{2,3}$ 6.4, J$_{2,6}$ 0.5)	67
5-CHO, 4-OH	7.55(d, H-2), 7.61(d, 3-H), 7.82(d, 6-H), 7.01(d, 7-H), 12.40(OH), (J$_{2,3}$ 5.95, J$_{6,7}$ 7.95, J$_{2,6}$ 0.4)	67
5-Allyl, 4-OH	7.23(d, H-2), 7.35(d, 3-H), 6.95(d, 6-H), 7.35(d, 7-H), 5.45(br, OH), (J$_{2,3}$ 5.85, J$_6$ 8.05, J$_{2,6}$ 0.5)	67
7-Ac, 4-OH^d	7.51(d, H-2), 6.85(d, 3-H), 8.05(d, 5-H), 3.4(br, OH), (J$_{2,3}$ 5.75, J$_{6,8}$ 7.85, J$_{2,6}$ 0.5)	67

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment	Ref.
4-OAc	7.32(d, 2-H), 7.43(d, 3-H), 7.05(dd, 5-H), 7.15(dd, 6-H), 7.69(dd, 7-H), ($J_{2,3}$ 5.9, $J_{6,8}$ 8.1, $J_{6,7}$ 8.0, $J_{2,6}$ 0.5)	67
3-Br, 4-OH	7.22(2-H), 6.85(dd, 5-H), 7.28(dd, 6-H), 7.45(dd, 7-H), ($J_{5,6}$ 7.85, $J_{6,7}$ 7.95, $J_{2,6}$ 0.5)	67
5-Br, 3-CH$_3$, 4-OH[e]	6.78(2-H), 7.46(d, 6-H), 7.18(d, 7-H), 5.15(OH), 2.35(3-Me), ($J_{6,7}$ 7.8, $J_{2,6}$ 0.15-0.8)	67
5, 7-Br$_2$, 3-CH$_3$, 4-OH	6.91(2-H), 7.42(6-H), 5.75(OH), 2.52(3-Me), ($J_{2,6}$ 0.5-0.8)	67
5-NO$_2$, 3-CH$_3$, 4-OH	7.01(2-H), 7.92(d, 6-H), 7.28(d, 7-H), 11.92(OH), 2.65(3-Me), ($J_{6,7}$ 8.05, $J_{2,6}$ 0.5-0.8)	67
5, 7-(NO$_2$)$_2$, 3-CH$_3$, 4-OH	7.68(2-H), 8.55(6-H), 11.59(OH), 239(3-Me), ($J_{2,6}$ 0.5-0.7)	67
5-CHO, 3-CH$_3$, 4-OH[e]	6.35(2-H), 6.92(d, 2-H), 6.55(d, 7-H), 12.69(OH), 2.51(3-Me), 9.28(CHO), ($J_{6,7}$ 8.15, $J_{2,6}$ 0.4-0.8)	67
5-Allyl, 3-CH$_3$, 4-OH	6.85(2-H), 7.02(d, 6-H), 7.35(d, 7-H), 5.45(OH), 2.65(3-Me), ($J_{6,7}$ 8.10, $J_{2,6}$ 0.4-0.8)	67
4-OAc, 3-CH$_3$, 4-OH	6.98(2-H), 6.91(dd, 5-H), 7.22(6-H), 7.55(d, 7-H), 2.40(3-Me), 2.25(OAc), ($J_{5,6}$ 8.0, $J_{6,7}$ 8.0, $J_{2,6}$ 0.5-0.8)	67
2-Ac, 3-CH$_3$, 4-OH	6.92(dd, 5-H), 7.32(6-H), 7.45(dd, 7-H), 3.40(OH), 2.60(Ac), 2.85(3-Me), ($J_{5,6}$ 7.85, $J_{6,7}$ 7.85)	67
7-Ac, 3-CH$_3$, 4-OH[d]	7.22(2-H), 6.85(d, 5-H), 8.05(d, 6-H), 3.38(OH), 2.58(3-Me), 2.50(Ac), ($J_{5,6}$ 8.25, $J_{2,6}$ 0.5-0.7)	67
2-Ac, 7-Cl, 3-CH$_3$	7.80-7.65(dd, 4-H or 6-H), 7.53-7.25(m, 5-H and 6-H or 4-H), 2.70(s, Ac), 2.60(s, 3-Me),	67
3-Me, 7-OH	7.43-7.23(m, 4-H and 5-H), 7.05(s, 2-H), 6.73(dd, 6-H), 5.21(s, OH), 2.38(s, 3-Me)	67
3-CH$_3$, 7-SH	7.57(dd, 4-H), 7.11(s, 2-H), 3.48(s, SH), 2.30(s, 3-Me)	67
3- $\overset{Ph}{\underset{\cdot}{C}}$ =NHCOPh	7.8(15H, m, aromatic protons), 9.05(1H, br, NH)	52
3- $\overset{Ph}{\underset{\cdot}{C}}$ HNHNHCOPh	4.74, 8.0 (each 1H, br, NH), 5.75 (1H, s, >CH), 7.0-8.0 (15H, m, aromatic protons)	52
3- $\overset{Ph}{\underset{\cdot}{C}}$ H-OH[b]	3.75(1H, br, OH), 5.62(1H, s, >CH), 6.90-7.80(10H, m, aromatic protons)	52
3- $\overset{Ph}{\underset{\cdot}{C}}$ =NNHCOPh, 2-CH$_3$	2.40(3H, s, CH$_3$), 7.0-8.2(14H, m, aromatic protons), 9.0(1H, br, NH)	52

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment	Ref.
3-Ph, 2-C=NNHCOPh (Ph)	7.0-8.2(19H, m, aromatic protons), 8.5(1H, br, NH)	52
2-Hexyl[b]	7.0-7.7(m, 4H, benzene ring protons), 6.8(s, 1H, 3-H), 2.8(t, 2H, CH_2-Ar), 1.1-1.9(br, m, 8H, central methylene protons), 0.9(t, 3H, CH_3)	72
5-Cl, 3-CHO	8.29(1H, s, 2-H), 8.58(1H, d, 4-H), $(J_{4,6}$ 2.0), 7.34(1H, dd, 6-H), $J_{4,6}$ 2), 7.70(1H, d, 7-H), $(J_{6,7}$ 8), 10.02(1H, s, CHO)	73
5-F, 3-CHO	8.36(1H, s, 2-H), 8.36(1H, dd, 4-H), $J_{4,6}$ 2.5, $J_{4,F}$ 9.5 7.21(1H, td, 6-H), $J_{4,6}$ 2.5, $J_{6,F}$ 8.5, $J_{6,9}$ 9), 7.79(1H, dd, 7-H), $J_{6,7}$ 9, $J_{7,F}$ 5), 10.08(1H, s, CHO)	73
5-CH_3, 6-OCH_3, 2-$COOCH_3$	2.30(s, 3H), 3.91(s, 3H), 3.93(s, 3H), 7.25(s, 1H), 7.63(s, 1H), 6.97(s, 1H)	41
5-CH_3, 6-OCH_3	2.30(s, 3H), 3.82(s, 3H), 7.23(s, 1H), 7.26(d, 2H, J, 2), 6.57(s, 1H)	41
6-CH_3, 5-OCH_3, 2-COOH	2.30(s, 3H), 3.90(s, 3H), 7.55(s, 1H), 7.83(s, 1H), 8.07(s, 1H)	41
6-CH_3, 5-OCH_3, 2-$COOCH_3$	2.38(s, 3H), 3.97(s, 3H), 4.02(s, 3H), 7.27(s, 1H), 7.67(s, 1H), 8.05(s, 1H)	41
6-CH_3, 5-OCH_3[b]	2.32(s, 3H), 3.90(s, 3H), 7.14-7.37(m, 3H), 7.58(s, 1H)	41
5-Cl, 3-Ph[b]	7.25(2-H), 7.80(d, 4-H, J 2.0), 7.67(d, 7-H, J 9.0), 7.25(dd, 6-H), 7.37(C_6H_5)	74
5-Br, 3-Ph[b]	7.25(2-H), 7.96(d, 4-H, J 1.8), 7.60(d, 7-H, J 8.5), 7.38(C_6H_5)	74
3-Br, 2-Ph, 5-CH_3[b]	7.80-6.95(m, Ar), 2.44(CH_3)	74
3, 5-Br_2, 2-Ph	8.04(d, 4-H, J 2.0)	74
3-Br, 5-Cl, 2-Ph[b]	7.80(d, 4-H, J 2.0)	74
1-Cyclohexanol, 3-Br	2.50-1.50(m, cyclohexane ring), 2.55(1H, OH, exchangable), 7.55-2.20(m, 5-H and 6-H), 7.90-2.65 (m, 4-H and 7-H)	74
2-Ph, 3-CHO[b]	7.80-7.10(m, 5-H, 6-H and 7-H), 8.73(m, 4-H), 7.40(C_6H_5), 9.97(CHO)	74
5-CH_3, 2-Ph, 3-CHO[b]	8.57(d, 4-H, J 1.7), 7.58(d, 7-H, J 8.2), 7.17(dd, 6-H), 2.50(CH_3), 7.45(C_6H_5), 9.99(CHO)	74
5-Br, 2-Ph, 3-CHO	7.80-7.50(m, 6-H, 7-H and C_6H_6), 9.11(d, 4-H, J 2.0), 10.06(CHO)	74

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment	Ref.
5-Cl, 2-Ph, 3-CHO	8.77(d, 4-H, J 2.0), 7.69(d, 7-H, J 8.5), 7.36(dd, 6-H), 7.52(C_6H_5), 9.98(CHO)	74
3-CH_3, 2-Ph[b]	2.32(CH_3), 7.80-7.10(m, Ar-H)	74
2, 3-Br_2, 5-Cl[d]	8.05(d, J 9.0, 7-H), 7.80(d, J 2.0, 4-H), 7.53(dd, 6-H)	75
3-Br, 5-Cl[b]	7.77(d, J 2.0, 4-H), 7.66(d, J 8.2, 7-H), 7.40(2-H), 7.30(dd, 6-H)	75
2, 3-Br_2, 5-CH_3[b]	7.44(d, J 8.0, 7-H), 7.43(d, J 1.7, 4-H), 7.08(dd, 6-H), 7.45(Me)	75
3-Br, 5-CH_3[h]	7.43(d, J 1.7, 4-H), 7.33(d, J 8.2, 7-H), 7.40(2-H), 6.80(dd, 6-H)	75
5-CH_3, 3-COCH[d]	8.65(2-H), 8.41(d, J 1.8, 4-H), 7.93(d, J 8.5, 7-H), 7.38(dd, 6-H)	75
5-Cl, 3-COOH[d]	8.80(2-H), 8.59(d, J 2.0, 4-H), 8.19(d, J 8.7, 7-H), 7.57(dd, 6-H)	75
5-CH_3, 3-CHO	8.28(2-H), 8.55(d, J 1.8, 4-H), 7.31(dd, 6-H), 7.77(d, J 8.2, 7-H), 2.52(Me), 10.17(CHO)	75
5-Cl, 3-CHO	8.35(2-H), 8.73(d, J 2.0, 4-H), 7.40(dd, 6-H), 7.75(d, J 8.7, 7-H), 10.15(CHO)	75
4-Bu^n, 5-NO[b]	0.8-2.25 and 5.10-4.35(7-H and 2-H, m, n-C_4H_9), 6.15-6.30 and 7.40-7.55(1H and 1H, AB system, 6-H, 7-H, J 8.5), 7.50-7.60 and 7.75-7.85(1H and 1H, AB system, 2-H, 3-H, J 6.0)	76
4-$(CH_2)_2$Ph, 5-NO[b]	3.05-3.35 and 4.35 - 4.65(2H and 2H, m, CH_2CH_2), 6.15-6.30 and 7.40-7.55(1H, 1H AB system, 6-H, 7-H, J 8.5), 8.10(1H and 1H, AB system, 4-H, 5-H, J 8.5), 8.10(1H,,5, 2-H)	76
3-$CH_2COOC_2H_5$	1.20(t, 3H, ester CH_3), 3.82(s, 2H, ArCH_2), 4.15(q, 2H, ester CH_2), 7.1-8.0(m, 5H, ArH)	77
3-CH_2CONH_2[d]	3.65(s, 2H, CH_2), 6.92(s, 1H, NH), 8.0-7.1(m, 6H, NH and ArH)	77
3-$CH_2CONHCH_3$	2.67(d, 3H, CH_3), 3.77)s, 2H, CH_3), 5.78(s, 1H, NH), 7.2-8.0(m, 5H, ArH)	77
3-$CH_2CH_2NH_2$	3.23(m, 4H, CH_2-CH_2), 7.2-8.2(m, 5H, ArH), 8.47(s, br, 3H, $R\overset{+}{N}H_3$)	77
3-$CH_2CH_2NHCH_3$	2.93(s, 3H, CH_3), 3.40(s, 4H, CH_2CH_2), 7.3-8.1(m, 5-H, ArH)	77
3-$CH_2CH_2N(CH_3)_2$	2.32(s, 6H, CH_3), 2.42-3.2(m, 4H, CH_2CH_2), 6.9-8.0(m, 5H, ArH)	77
3-CH_2NH_2	4.63(s, 2H, CH_2), 7.8-8.2(m, 5H, ArH)	77
3-$CH_2N(CH_3)_2$	2.98(s, 6H, CH_3), 4.57(s, 2H, CH_3), 7.3-8.1(ArH)	77

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment	Ref.
4-OCH$_3$, 3-CH$_2$CH$_2$N(CH$_3$)$_2$	6.92(2-H), 6.65(dd, 5-H), 7.17(q, 6-H), 7.33(dd, 7-H), 3.84(OCH$_3$) (J$_{7,5}$ 1.6, J$_{6,7}$ 7.5)	36
4-OCH$_3$, 2-CHO	8.10(s, 3-H), 6.70(m, 5-H), 7.32(m, 7-H), 3.94(OCH$_3$)	36
4-OCH$_3$, 2-Me	7.06(m, 3-H), 6.55(dd, 5-H), 7.10(q, 6-H), 7.24(dd, 7-H), 3.76(s, OCH$_3$), 2.44(d, 2-Me), (J$_{2,3}$ 1.0, J$_{5,6}$ 7.8, J$_{5,7}$ 1.0, J$_{6,7}$ 8.0)	36
7-OCH$_3$, 4-OH	6.98(m, 2-H), 7.27(4-H), 7.27(5-H), 6.71(m, 6-H), 3.93(s, 7-OCH$_3$), 2.38(d, 3-CH$_3$), (J$_{2,3}$ 1.1)	36
5-Ac, 4-OH	2.65(s, 5-Ac), 10.75(s, OH), 7.23(d, 7-H), 7.31(d, 2-H), 7.51(d, 6-H), 7.60(d, 3-H), (J$_{2,3}$ 5.5, J$_{6,7}$ 8.5, J$_{3,7}$ 0.7, J$_{2,6}$ 0.5)	78
3-Ac, 6-OH, 2-Ph	2.40(s, Ac), 7.01(dd, 5-H), 7.24(d, 7-H), 7.43(s, Ph), 8.09(d, 4-H), (J$_{4,5}$ 8.2, J$_{5,7}$ 1.8)	78
6-OAc, 3-Ac	2.31(s, OAC), 2.62(s, AC), 7.21(dd, 5-H), 7.61(d, 7-H), 8.22(s, 2-H), 8.75(d, 4-H), (J$_{4,5}$ 8.7, J$_{5,7}$ 2.2)	78
6-OAc, 2-Ac	2.32(s, OAC), 2.62(s, AC), 7.10(dd, 5-H), 7.55(dd, 7-H), 7.86(d, 4-H), 7.92(d, 3-H), (J$_{4,5}$ 8.5, J$_{5,7}$ 1.9, J$_{3,7}$ 0.6)	78
4-Ac, 7-OH[d]	2.55(s, AC), 6.85(d, 6-H), 7.35(d, 2-H), 7.80(d, 5-H), 7.97(d, 3-H), (J$_{2,3}$ 5.8, J$_{5,6}$ 7.9)	78
5-NH$_2$, 4-Br, 3-CH$_3$, 2-COOEt	7.49(d, 7-H), 6.91(d, 6-H), 4.0(br, s, NH$_2$), 3.1(d, 3-Me), (J$_{6,7}$ 8)	64
4-Br, 3-CH$_3$, 2-COOEt	7.74(dd, 5-H), 7.6(dd, 7-H), 7.21(t, 6-H), 3.1(s, 3-Me), (J$_{5,6}$ 8, J$_{6,7}$ and J$_{5,7}$ 2)	64
3-CH$_3$, 5-COOEt	8.25(dd, 4-H), 7.90(dd, 6-H), 7.68(dd, 7-H), 6.90(q, 2-H), 4.35(q, CH$_3$-CH$_2$), 2.33(d, ArCH$_3$), 1.32(t, CH$_3$CH$_2$), (J$_{2,3}$ 1.2, J$_{4,6}$ 1.6, J$_{4,7}$ 0.6, J$_{6,7}$ 8.5)	64
3-CH$_2$Br, 2-COOEt	8.05-7.40(m, 4, 5, 6, 7-H), 5.2(s, 3-CH$_2$Br)	64
3-CH$_2$Br, 4-Br, 2-COOEt	7.77(q, 5-H), 7.67(dd, 7-H), 2.29(6-H), 5.64(s, 3-CH$_2$Br), (J$_{5,6}$ 8, J$_{6,7}$ 8 and J$_{5,7}$ 1)	64
3-CH$_2$Br$_2$, 5-Br, 2-COOEt	7.68(d, 6-H), 7.69(d, 7-H), 5.65(s, 3-CH$_2$Br), (J$_{6,7}$ 8)	64
3-CH$_2$Br, 5-COOEt, 2-COOEt	8.58(dd, 4-H), 8.08(dd, 6-H), 7.88(dd, 7-H), 7.00(t, 2-H), 4.74(s, 3-CH$_2$Br), (J$_{2,3}$ 1.1, J$_{4,6}$ 1.4, J$_{4,7}$ 1.0, J$_{6,7}$ 8.5)	64

TABLE 5 (Contd.)

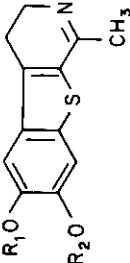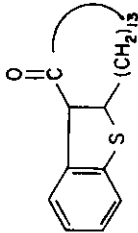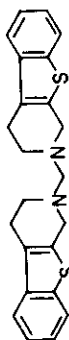| Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J in Hz, Assignment	Ref.
3-CH$_3$, 7-OSO$_2$Me	7.75-7.57(m 4-H9, 7.5-7.3(m, 5-H and 6-H), 7.12(s, 2-H), 3.19(s, SO$_2$Me), 2.42(s, 3-Me)	69
7-OH, 3-CH$_2$CN[d]	7.66(s, 2-H), 7.35-7.25(m, 4-H and 5-H), 6.85(q, 6-H), 4.20(s, CH$_2$CN)	69
5-OH, 3-CH$_2$COOCH$_3$	7.62(d, 7-H), 7.31(s, 2-H), 7.15(d, 4-H), 6.89(dd, 6-H), 6.14(s, OH), 3.76(s, 3-CH$_2$), 3.65(s, CH$_3$)	69
5-OH, 3-CH$_2$CONH$_2$	7.70(d, 7-H), 7.49(br, s, OH), 7.42(s, 2-H), 7.17(d, 4-H), 6.95(br, s, NH$_2$), 6.89(dd, 6-H), 3.54(s, 3-CH$_2$), (J$_{4,6}$ 2.5, J$_{6,7}$ 8.3)	69
7-Br, 4-OCH$_3$, 3-CH$_3$	2.55(d, 3-Me), 3.85(s, OMe), 6.55(d, 5-H), 6.9(q, 2-H), 7.3(d, 6-H), (J$_{2,3-Me}$ 0.8, J$_{5,6}$ 8.0)	34
2-Br, 4-OCH$_3$, 3-CH$_3$	2.6(s, 3-Me), 3.95(s, OMe), 6.75(dd, 5-H), 7.26(t, 6-H), 7.36(dd, 7-H), (J$_{5,6}$ = J$_{6,7}$ = 8.0, J$_{5,7}$ 2.0)	34
4-OCH$_3$, 2, 7-Br$_2$, 3-CH$_3$	2.65(s, 3-Me), 4.0(s, OMe), 6.6(d, 5-H), 7.3(d, 6-H), (J$_{5,6}$ 8.0)	34
4-OCH$_3$, 3-CH$_3$, 2-NO$_2$	3.05(s, 3-Me), 3.95(s, OMe), 6.8(dd, 5-H), 7.32(t, 6-H), 7.49(dd, 7-H), (J$_{5,6}$ = J$_{6,7}$ = 8.0, J$_{5,7}$ 1.8)	34
4-OCH$_3$, 3-CH$_3$, 7-NO$_2$	2.65(d, 3-Me), 4.0(s, OMe), 6.77(d, 5-H), 7.05(q, 2-H), 8.33(d, 6-H), (J$_{2,3-Me}$ 0.8, J$_{5,6}$ 8.0)	34
4-OCH$_3$, 2, 7-(NO$_2$)$_2$[d]	4.14(s, OMe), 7.35(d, 5-H), 8.45(s, 3-H), 8.7(d, 6-H), (J$_{5,6}$ 8.0)	34
4-OCH$_2$, 3-CH$_3$, 2,7-(NO$_2$)$_2$	3.05(s, 3-Me), 4.15(s, OMe), 6.96(d, 5-H), 8.55(d, 6-H), (J$_{5,6}$ 8.0)	34
4-OCH$_3$, 3-CH$_3$, 2-CHO	2.9(s, 3-Me), 3.9(s, OMe), 6.9(diffuse dd, 5-H), 7.35(m, 6-H and 7-H), 10.22(s, CHO)	34
4-OCH$_3$, 3-CH$_3$, 7-CHO	2.55(d, 3-Me), 3.95(s, OMe), 6.82(d, 5-H), 7.0(q, 2-H), 7.7(d, 6-H), 10.01(s, CHO), (J$_{2, 3-Me}$, J$_{5,6}$ 8.0)	34
2-COCH$_3$, 4-OCH$_3$, 3-CH$_3$	2.55(s, AC), 2.92(s, 3-Me), 3.88(s, OMe), 6.96(diffuse dd, 5-H), 7.3(m, 6-H and 7-H)	34
7-COCH$_3$, 4-OCH$_3$, 3-CH$_3$	2.54(s, AC), 2.6(d, 3-Me), 3.9(s, OMe), 6.65(d, 5-H), 6.98(q, 2-H), 7.28(d, 6-H), (J$_{2, 3-Me}$ 0.8, J$_{5,6}$ 8.0)	34
2-COCH$_3$ 7-Cl, 4-OCH$_3$, 3-CH$_3$	2.95(s, 3-Me), 3.90(s, OMe), 6.72(d, 5-H), 7.34(d, 6-H), (J$_{5,6}$ 8.0)	34

TABLE 5 (Contd.)

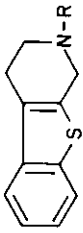| Substituents	Chemical shift δ (ppm), Multiplicity, Coupling Constant J(Hz), Assignment	Ref.
4-NH$_2$, 5-N(C$_2$H$_5$)$_2$, 2-COOC$_2$H$_5$	8.13(1H, s, 3-H), 7.27(2H, s, 6-H and 7-H), 4.79(s, br, exchangeable, NH$_2$), 4.42(2H, q, J 7.0, ester CH$_2$), 2.98(4H, q, J 7.0, CH$_2$), 1.40(3H, t, J 7.0, ester CH$_3$), 0.99(6H, t, J 7.0, CH$_3$)	59
4-N(COCH$_3$)$_2$, 5-N(C$_2$H$_5$)$_2$, 2-COOC$_2$H$_5$	7.85 and 7.35(2H, d, aromatic, 6-H and 7-H), 7.72(1H, s, 3-H), 4.43(2H, q, J 7.0, ester CH$_2$), 3.05(4H, q, J 7.0, CH$_2$), 2.32(6H, s, acetyl CH$_3$), 1.40(3H, t, J 7.0, ester CH$_3$), 1.04(6H, t, J 7.0, CH$_3$)	59
4-NH$_2$, 5-piperidine, 2-COOC$_2$H$_5$	8.11(1H, s, 3-H), 7.26(2H, s, 6-H and 7-H), 4.60(2H, s, exchangeable, NH$_2$), 4.43(2H, q, J 7.0, ester CH$_2$), 1.40(3H, t, J 7.0, CH$_3$), 2.85(br, 4H, m, CH$_2$), 1.65(br, 6H, m, - and -, CH$_2$)	59
5-Ph, 2-COOC$_2$H$_5$	8.45-7.40(9H, m, aromatic), 4.40(2H, q, J 7.0, CH$_2$), 1.40(3H, q, J 7.0, CH$_3$)	59
5-N(C$_2$H$_5$)$_2$, 2-COOC$_2$H$_5$ [b]	7.85(m, 3-H and 7-H), 7.50(q, $J_{4,6}$ 2.0, $J_{4,7}$ <1.0, 4-H), 6.95(q, $J_{4,6}$ 2.0, $J_{6,7}$ 10.0, 6-H), 4.31(2H, q, J 7.0, ester CH$_2$), 3.34(4H, q, J 6.5, CH$_2$), 1.34(3H, t, J 7.0, ester CH$_3$), 1.10(6H, t, J 6.5, CH$_3$)	59
5-Acetamido, 4-NO$_2$, 2-COOC$_2$H$_5$	8.65(1H, s, 3-H), 8.49 and 8.24(2H, d, 6-H and 7-H), 4.66(2H, q, J 7.0, CH$_2$), 1.56(3H, t, J 7.0, CH$_3$), 2.50(3H, s, amide CH$_3$)	59
5-NH$_2$, 4-NO$_2$, 2-COOC$_2$H$_5$ [b]	8.79(1H, s, 3-H), 7.78 and 7.19(2H, d, 6-H and 7-H, $J_{6,7}$ 10.0), 4.43(2H, q, J 7.0, CH$_2$), 1.45(3H, t, J 7.0, CH$_3$)	59
5-NHC$_2$H$_5$, 4-NO$_2$, 2-COOC$_2$H$_5$	9.00(s, br, 1H, NH), 8.91(1H, s, 3-H), 7.84 and 7.06(2H, d, 6-H and 7-H, $J_{6,7}$ 10.0), 4.49(2H, q, J 7.0, ester CH$_2$), 3.49(2H, q, J 6.0, amine CH$_2$), 1.43(6H, t, J 7.0, 2 x Me)	59
OCH$_3$ | 2-CH-COOH [d]	7.96-7.75(4, 5, 6 and 7-H), 7.50(3-H), 5.30(CH), 3.50(CH$_3$), 10.13(COOH)	70

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant J(Hz), Assignment	Ref.
OCH$_3$ | 3-CH-COOH[d]	7.80(2-H), 8.33-7.33(4, 5, 6 and 7-H), 5.33(C-H), 3.56(CH$_3$)	70
3-CH-COOH[d] | Br	8.75-7.33(4, 5, 6 and 7-H), 8.03(2-H), 6.10(C-H), 10.00(COOH)	70
3-Br, 2-CH$_2$COOH[d]	7.05(4, 5, 6 and 7-H), 4.05(CH$_2$), 10.25(COOH)	70
3-Br, 2-CH$_2$COOCH$_3$[d]	4.03(CH$_2$), 3.70(CH$_3$)	70
2-CH$_2$Br[d]	7.19-7.16(4, 5, 6 and 7-H), 7.41(3-H), 4.91(CH$_2$)	70
2-CH$_2$Cl[d]	8.0-7.97(4, 5, 6 and 7-H), 7.38(3-H), 5.0(CH$_2$)	70
3-COOH[d]	8.14-7.41(4, 5, 6 and 7-H), 8.63(2-H)	70
3-CH$_2$Br[d]	8.08-7.33(4, 5, 6 and 7-H), 7.75(2-H), 4.90(CH$_2$)	70
4-OCH$_2$Ph, 3-Me, 2-COOH[d]	2.95(s, Me)	70
4-OCH$_2$Ph, 3-CH$_3$	2.6(d, Me), 7.15(q, 2-H), (J$_{2,3-Me}$ 0.7)	70
3-CH$_3$, 4-OCH$_3$	3.85(s, OMe), 6.8(q, 2-H), 2.6(d, Me), (J$_{2,3-Me}$ 0.8)	70
3-CH$_2$Br, 4-OCH$_3$	7.05(s, 2-H), 4.65(s, CH$_2$Br), 3.75(s, OMe)	70
4-OCH$_3$, 3-CH$_2$CN	4.15(CH$_2$CN)	70
3-CHO[d]	8.58-7.41(4, 5, 6 and 7-H), 8.66(2-H), 10.16(CHO)	70
4-OCH$_3$, 3-CH$_2$COOH	4.0(s, CH$_2$COOH)	71
4-OCH$_3$, 3-CH$_2$CONMe$_2$	3.95(s, CH$_2$CO), 3.0 and 2.85(CONMe$_2$)	71
4-OH, 3-CH$_2$COOH[d]	3.95(s, CH$_2$)	71
4-OH, 3-CH$_2$CONMe$_2$	2.95 and 3.2(s, NMe$_2$), 4.15(s, CH$_2$CO)	71
4-OH, 3-CH$_3$	2.6(s, Me, 5.1(OH)	71
4-NH$_2$, 5-N(C$_2$H$_5$)$_2$[e]	7.35-6.85(4H, m, aromatic), 4.00(br, s, 2H, exchangeable, NH$_2$), 2.78(4H, q, J 7.0, CH$_2$), 0.91(6H, t, J 7.0, CH$_3$)	59

TABLE 5 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant J(Hz), Assignment	Ref.
4-N(COCH$_3$)$_2$, 5-N(C$_2$H$_5$)$_2$	7.89 and 7.24(2H, d, aromatic, J 9.0, 6-H and 7-H), 7.52 and 7.02(2H, d, aromatic, J 6.0, 2-H and 3-H), 5.06(4H, q, J 7.0, CH$_2$), 1.06(6H, t, J 7.0, CH$_3$), 2.32(6H, s, acetyl CH$_3$)	59
4-NH$_2$, 5-morpholino	7.45-7.10(4H, m, aromatic), 5.50(br, s, 2H, exchangeable, NH$_2$), 4.0-3.80(4H, m, OCH$_2$), 3.05-2.85(4H, m, NCH$_2$)	59
5-OH, 3-CH$_2$$\overset{\overset{\text{NH}_2}{\mid}}{\text{CH}}$COOH[i]	7.58(2-H), 7.28(4-H), 7.09(6-H), 7.79(7-H), 3.55(m, CH$_2$), 4.54(t, →CH)	79
5-OCH$_3$, 3-CH$_2$CN[i]	7.39(2-H), 7.04(4-H), 7.00(6-H), 7.68(7-H), 3.75(d, CH$_2$)	79
5-OH, 3-CH$_2$CH$_2$NH$_2$	7.45(2-H), 7.29(4-H), 7.10(6-H), 7.74(7-H), 3.38(m, CH$_2$CH$_2$)	79
5-OCH$_3$, 3-CH$_2$CH$_2$NH$_2$[i]	7.54(2-H), 7.41(4-H), 7.09(6-H), 7.82(7-H), 3.33(m, CH$_2$CH$_2$), 3.95(OCH$_3$)	79
5-OH, 3-CH$_2$CH$_2$NHCOCH$_3$	7.29(2-H), 7.35(4-H), 6.92(6-H), 7.67(7-H), 2.99(7, ArCH$_2$), 3.42(q, 2H, CH$_2$NHCOCH$_3$)	79
5-OCH$_3$, 3-CH$_2$CH$_2$NHCOCH$_3$	7.12(2-H), 7.22(4-H), 7.0(6-H), 7.68(7-H), 3.02(m, ArCH$_2$), 3.58(m, 2H, CH$_2$NHCOCH$_3$)	79
5-OH, 3-CH$_2$COOH[i]	7.46(2-H), 7.27(4-H), 7.00(6-H), 7.70(7-H), 3.84(CH$_2$)	79
5-OCH$_3$, 3-CH$_2$COOH[i]	7.50(2-H), 7.35(4-H), 7.00(6-H), 7.75(7-H), 3.86(s, CH$_2$), 3.86(OCH$_3$)	79
5-OH, 3-CH$_2$CON(CH$_3$)$_2$	7.35(2-H), 7.13(4-H), 6.86(6-H and 7-H), 3.80(s, CH$_2$), 9.36(NCH$_3$)$_2$	79
5-OCH$_3$, 3-CH$_2$CON(CH$_3$)$_2$	7.19(2-H), 7.27(4-H), 6.98(6-H), 7.66(7-H), 3.84(s, CH$_2$), 3.87(OCH$_3$)	79
5-OCH$_3$, 3-CH$_2$CON(C$_2$H$_5$)$_2$	7.18(2-H), 7.26(4-H), 6.96(6-H), 7.64(7-H), 3.81(d, CH$_2$), 3.87(OCH$_3$)	79
5-OCH$_3$, 3-CH$_2$CONHCH$_3$	7.29(2-H), 7.14(4-H), 7.00(6-H), 7.70(7-H), 3.77(s, CH$_2$), 3.85(OCH$_3$)	79
5-OH, 3-CH$_2$CH$_2$N(CH$_3$)$_2$	7.41(2-H), 7.31(4-H), 7.02(6-H), 7.68(7-H), 3.54(t, CH$_2$CH$_2$)	79
5-OCH$_3$, 3-CH$_2$CH$_2$NHCH$_3$	7.47(2-H), 7.35(4-H), 6.97(6-H), 7.62(7-H), 3.36(t, CH$_2$CH$_2$), 3.95(NHCH$_3$)	79

TABLE 5 (Contd.)

Substitutents	Chemical Shift δ (ppm), Multiplicity, Coupling Constant, J(Hz), Assignment	Ref.
a. $R_1 = H$, $R_2 = CH_3$	7.30(s, 1H), 7.22(s, 1H), 5.80(s, 1H), 4.00(s, 3H), 3.84(t, 3H), 2.38(s, 3H)	62
b. $R_1 = CH_3$, $R_2 = H$	7.32(s, 1H), 7.24(s, 1H), 5.75(s, 1H), 3.95(s, 1H), 3.82(t, 2H), 3.05(t, 2H) 2.40(s, 3H)	62
c. $R_1 = R_2 = (CH_3)_2$	7.05(s, 1H), 6.92(s, 1H), 3.80(t, 2H), 2.75(t, 2H), 2.33(s, 3H), 1.64(s, 6H)	62
d. $R_1 = R_2 = H^b$	7.48(s, 1H), 7.30(s, 1H), 3.92(t, 2H), 3.20(t, 2H), 2.66(s, 3H)	62
	7.07-7.7(m, 4, 5, 6 and 7-H), 2.85(t, 2H, ArCH$_2$), 2.70(t, 2H, CH$_2$COAr), 1.0-1.8(br, m, 22H) (central methylene protons)	72
	2.63-3.32(m, 8H, CH$_2$CH$_2$), 3.42(s, 2H, N-CH$_2$-N), 3.90(m, 4H, ArCH$_2$-N), 7.0-7.9(m, 8H, ArH)	77
	2.50(s, 3H, CH$_3$), 2.83(m, 4H, CH$_2$CH$_2$), 3.68(m, 2H, ArCH$_2$N), 7.1-7.9(m, 4H, ArH), 2.9-3.9(m, 4H, ArCH$_2$CH$_2$N), 3.20(s, 3H, NCH$_3$), 3.44(m, 2H, ArCH$_2$N), 7.4-8.2(m, 4H, ArH)	77

a. In CDCl$_3$, unless otherwise indicated. b. carbon tetrachloride d. (CD$_3$)$_2$SO.

e. C$_6$D$_6$ j. (CD$_3$)$_2$CO i. DMSO$_4$-d$_6$ k. Chemical shifts referred to cyclohexane

— 1254 —

TABLE 6

R_1O — [benzothiophene ring structure] — CH_2R
R_2O — S
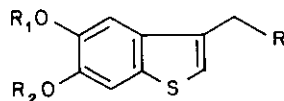
Compound	Chemical Shift δ (ppm)[a], Multiplicity	Ref.
$R_1 = R_2 = OCH_3$, $R = COOC_2H_5$	1.23(t, 3H, ester CH_3), 3.80(s, 2H, $ArCH_2$), 3.97(s, 6H, 2 x OCH_3), 4.17(q, 2H, ester CH_2) 7.23(m, 3H, ArH)	62
$R_1 = H$, $R_2 = CH_3$, $R = COOC_2H_5$	1.27(t, 3H, ester CH_3), 3.77(s, $ArCH_2$), 3.90(s, 3H, 6-OCH_3), 4.20(q, 2H, ester CH_2) 7.23(m, 3H, ArH), 5.83(s, 1H, OH, exchangeable)	62
$R_1 = H$, $R_2 = CH_3$, $R = COOCH_3$	7.23(1H), 7.15(s, 2H), 6.12(s, 1H), 3.79(s, 3H), 3.72(s, 2H), 3.62(s, 3H)	62
$R_1 = CH_2OCH_3$, $R_2 = CH_3$ $R = COOC_2H_5$	7.60(s, 1H), 7.40(s, 1H), 7.30(s, 1H), 5.35(s, 2H, CH_2OCH_3), 4.25(q, ester CH_2) 4.0(s, 5-OCH_3), 3.85(s, $ArCH_2$), 3.60(s, 6-OCH_3), 1.33(t, ester CH_3)	62 62
$R_1 = CH_2OCH_3$, $R_2 = CH_3$, $R = COOCH_3$	7.61(s, 1H), 7.40(s, 1H), 7.29(s, 1H), 5.35(s, 2H), 3.98(s, 3H), 3.81(s, 2H), 3.70(s, 3H) 3.60(s, 3H)	62
$R_1 = CH_3$, $R_2 = H$, $R = COOCH_3$	7.30(s, 1H), 7.10(s, 2H), 6.25(s, OH), 3.80(s, 3H), 3.70(sm 2H), 3.63(s, 3H)	62
$R_1 = CH_3$, $R_2 = CH_2OCH_3$, $R = COOCH_3$	7.60(s, 1H), 7.20(s, 2H), 5.25(s, 2H), 3.92(s, 3H), 3.77(s, 2H), 3.66(s, 3H), 3.50(s, 3H)	62
$R_1 = R_2$ $(CH_3)_2C$, $R = COOC_2H_5$	7.13(m, 3H, ArH), 3.75(s, $ArCH_2$), 4.18(q, ester CH_2), 1.27(t, ester CH_3), 1.70(s, 6H, $(CH_3)_2C$)	62
$R_1 = R_2 = H$, $R = COOC_2H_5$	7.13(m, 3H, ArH), 3.77(s, 2H, $ArCH_2$), 6.43(s, br, 2H, PhOH), 4.23(q, ester CH_2), 1.27(t, 3H, ester CH_3)	62
$R_1 = R_2 = C_4H_9{}^n$, $R = COOC_2H_5$	7.27(s, 1H), 7.13(s, 1H), 7.10(s, 1H), 4.30-3.90(m, 6H), 3.68(s, 2H), 2.12-1.90(m, 17H)	62
$R_1 = R_2 = C_4H_9{}^n$, $R = COOH$	7.35(s, 1H), 7.25(s, 2H), 8.45(s, 1H), 4.10(t, 4H), 3.82(s, 2H), 2.1-1.85(m, 14H)	62
$R_1 = H$, $R_2 = CH_3$, $R = CONH_2$	7.25-7.52(m, 4H), 9.08(s, 1H, OH), 6.97(s, 1H), 3.87(s, 3H), 3.53(s, 2H)	62

TABLE 6 (Contd.)

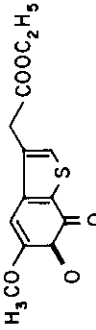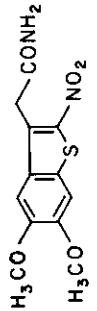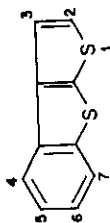| Compound	Chemical Shift δ (ppm)[a], Multiplicity	Ref.
$R_1 = CH_2OCH_3$, $R_2 = CH_3$,	7.60(s, 1H), 7.55(s, 1H), 7.50(s, 1H), 7.32(s, 1H), 7.00(s, 1H)	62
$R = CONH_2$[d]	5.20(s, 2H), 3.88(s, 3H), 3.60(s, 2H), 3.44(s, 3H)	62
$R_1 = CH_3$, $R_2 = H$, $R = COOC_2H_5$	1.23(t, 3H, ester CH_3), 3.77(s, 2H, $ArCH_2$), 3.90(s, 3H, $ArOCH_3$), 4.17(q, 2H, ester CH_2)	63
	9.8 (s, 1H, OH), 7.20(m, 3H, ArH)	
$R_1 = CH_3$, $R_2 = CH_2OCH_3$	7.57(s, 1H), 7.48(s, 1H), 7.33(s, 1H), 7.28(s, 1H), 6.90(s, 1H), 5.15(s, 2H), 3.78(s, 3H)	62
$R = CONH_2$[d]	3.52(s, 2H), 3.33(s, 3H)	
$R_1 = R_2 = H$, $R = CONH_2$[d]	3.55(s, 2H, CH_2), 6.93(s, 1H, NH), 7.18(m, 3H, ArH), 7.40(s, 1H, NH), 8.97(s, 2H, OH)	62
$R_1 = R_2 = n-C_4H_9$ $R = CONH_2$[d]	7.44(s, 1H), 7.40(s, 1H), 7.30(s, 1H), 5.63(s, 2H), 4.18(t, 4H), 3.90(s, 2H),	62
	2.18-1.15(m, 14H)	
$R_1 = R_2 = CH_3$, $R = CH_2NH_2$	7.20(s, 1H), 6.95(s, 1H), 6.8(s, 1H), 3.8(s, 6H), 2.5(m, 4H)	62
$R_1 = H$, $R_2 = CH_3$, $R = CH_2NH_2$[i]	7.48(s, 1H), 7.27(s, 1H), 7.20(s, 1H), 3.90(s, 3H), 3.60(t, 2H), 3.22(t, 2H)	62
$R_1 = CH_3$, $R_2 = H$, $R = CH_2NH_2$[i]	7.53(s, 1H), 7.42(s, 1H), 7.35(s, 1H), 4.02(s, 3H), 3.60-3.10(m, 4H)	62
$R_1 = R_2$, C_4H_9-n, $R = CH_2NH_2$	7.31-7.12(3H, ArH), 4.15(t, 4H), 3.65(t, 2H), 2.98(t, 2H), 2.10-1.95(m, 14H)	62
$R_1 = R_2 = CH_3$, $R = CH_2NHCONH_3$	7.3(s, 1H), 7.25(s, 1H), 7.0(s, 1H), 5.68(s, 1H), 3.92(s, 6H), 3.52(t, 2H), 1.9(s, 3H)	62
$R_1 = CH_2OCH_3$, $R_2 = CH_3$,	7.6(s, 1H), 7.42-7.10(m, 3H), 5.3(s, 2H), 4.0(s, 3H), 3.70(t, 2H), 3.60(s, 3H)	62
$R = CH_2NHCOCH_3$	3.70(t, 2H), 3.60(s, 3H), 3.10(t, 2H), 2.00(s, 3H)	62
$R_1 = H$, $R_2 = CH_3$, $R = CH_2NHCOCH_3$	7.25(s, 2H), 7.0(s, 1H), 5.00(s, 2H), 3.95(s, 3H), 3.50(t, 2H), 2.90(t, 2H), 2.10(s, 3H)	62
$R_1 = CH_3$, $R_2 = CH_2OCH_3$,	7.70(s, 1H), 7.35(s, 1H), 7.11(s, 1H), 5.80(s, 1H), 5.33(s, 1H), 4.05(s, 2H), 3.60(s, 3H)	62
$R = CH_2CONHCH_3$	3.59(t, 2H), 3.10(t, 2H), 2.05(s, 3H)	62
$R_1 = CH_3$, $R_2 = H$, $R = CH_2CONHCH_3$	7.32(s, 1H), 7.28(s, 1H), 7.10(s, 1H), 8.03(s, OH), 4.70(s, 1H), 3.88(s, 3H), 3.55(t, 2H),	62
	2.80(t, 2H), 1.80(s, 3H)	

TABLE 6 (Contd.)

| Compound	Chemical Shift δ (ppm)[a], Multiplicity	Ref.
$R_1 = R_2 = (CH_3)_2C$, $R = CH_2CONHCH_3$	7.27(s, 1H), 7.10(s, 1H), 7.0(s, 1H), 5.72(s, 1H), 3.60(q, 2H), 3.00(t, 2H), 2.00(s, 3H9, 2.72(s, 6H)	62
(structure with COOC$_2$H$_5$, H$_3$CO)	1.28(t, 3H, ester CH$_3$), 3.57(s, 2H, ArCH$_2$), 3.88(s, 3H, OCH$_3$), 4.20(q, 2H, ester CH$_2$), 6.42(s, 1H, ArH), 6.50(s, 1H, ArH)	62
(structure with CONH$_2$, NO$_2$, H$_3$CO)	4.08(s, 6H, OCH$_3$), 4.53(s, 2H, CH$_2$), 7.33(s, 1H, ArH), 7.47(s, 1H, ArH)	62

TABLE 7

Substituents	Chemical Shift δ (ppm)[a], Multiplicity, Coupling Constant J (Hz)	Ref.
2-Br, 3-CH$_3$	2.55(s, Me)	60
2-COCH$_3$, 3-CH$_3$	2.52(s, Me), 2.95(s, Ac)	60
3-CH$_3$, 2-CHO	2.9(s, Me), 9.95(s, CHO)	60
2-CH$_3$	2.55(d, Me), 2.85(q, 3-H), ($J_{2,3}$ 1.1 Hz)	60
3-Br, 2-CH$_3$	2.50(s, Me)	60
6-COCH$_3$, 2-CH$_3$	2.58(d, Me), 2.68(s, Ac), 7.18(q, 3-H), 7.82(dd, 4-H), 7.94(dd, 5-H), 8.38(dd, 7-H), ($J_{2,3}$ 1.1, $J_{4,6}$ 8.2, $J_{5,7}$ 1.6, $J_{4,7}$ 0.6)	60

TABLE 7 (Contd.)

Substituents	Chemical Shift δ (ppm)[a], Multiplicity, Coupling Constant J(Hz)	Ref.
3-COCH$_3$, 2-CH$_3$	2.65(s, Me), 2.67(s, Ac)	60
5-Br, 2-CHO	9.91(s, CHO)	60
5-Br, 2-CH$_3$	2.57(d, Me), 7.1(q, 3H), ($J_{2,3}$ 1.1)	60
5-CN, 2-CH$_3$	2.61(d, Me), 7.1(q, 3-H), ($J_{2,3}$ 1.1)	60
5-COCH$_3$, 2-CH$_3$	2.57(d, Me), 2.61(s, Ac), 7.40(q, 3-H), 7.79(dd, 6-H), 8.03(7-H), 8.55(dd, 4-H), ($J_{2,3}$ 1.1, $J_{6,7}$ 8.0, $J_{4,6}$ 1.5, $J_{4,7}$ 0.6)	60
3-CH$_2$Br, 2-CH$_3$	2.52(s, Me), 4.55(s, 2H, CH$_2$Br)	60
6-Br, 3-CH$_2$Br, 2-CH$_3$	2.54(s, Me), 4.57(s, 2H, CH$_2$Br), 7.53(dd, 5-H), 2.92(dd, 7-H), 7.95(dd, 4-H), ($J_{4,5}$ 8.5, $J_{5,7}$ 1.6, $J_{4,7}$ 0.5)	60
2-CH$_3$, 3-CHO	2.8(s, Me), 10.25(s, CHO)	60
6-COCH$_3$, 2, 3-(CH$_3$)$_2$	2.32(s, 2 x Me), 2.52(s, Ac)m 7.93(dd, 5-H), 8.00(dd, 4-H), 8.37(dd, 7-H), ($J_{7,8}$ 8.2, $J_{5,7}$ 1.4, $J_{5,8}$ 0.5)	60
2-Br, 3-CHO	10.15(s, CHO)	60
2-COCH$_3$	2.6(s, COMe), 8.0(s, 3-H)	61
2-CHO	10.09(s, CHO), 8.08(s, 3-H)	61
2-CN	8.0(s, 3-H)	61
2-NO$_2$	8.35(s, 3-H)	61
2-Acetamido	2.15(s, 3H, COMe)	61
2-CH$_2$OH	4.87(s, 2H, CH$_2$), 1.96(s, 1H, OH)	61

a = CDCl$_3$

TABLE 8
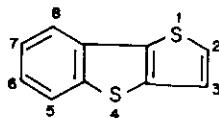
Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constants J (Hz)	Ref.
2-Br, 3-CH$_3$	2.50(s, Me)	60
2-COCH$_3$, 3-CH$_3$	2.55(s, Me), 2.65(s, Ac)	60
3-CH$_3$, 2-CHO	2.68(s, Me), 9.02(s, CHO)	60
2-CH$_3$	2.60(d, Me), 6.98(q, 3-H), (J$_{2,3}$ 1.0 Hz)	60
3-Br, 2-CH$_3$	2.52(s, Me)	60
2-CH$_3$, 3, 6(COCH$_3$)$_2$	2.62(s, Me), 2.80(s, 2 x Ac), 7.80(dd, 8-H), 7.99(dd, 7-H), 8.41(dd, 5-H), (J$_{7,8}$ 8.2, J$_{5,7}$ 1.2, J$_{5,8}$ 0.6)	60
3-COCH$_3$, 2-CH$_3$	2.62(s, Me), 2.85(s, Ac)	60
6-COCH$_3$, 2-CH$_3$	2.64(6H, m, Me and Ac), 7.0(q, 3-H), 7.75(dd, 8-H), 7.98(dd, 7-H), 8.44(dd, 5-H), (J$_{2,3}$ 1.1, J$_{7,8}$ 1.5, J$_{5,8}$ 0.5)	60
7-Br, 3-CH$_2$, Br, 2-CH$_3$	2.58(s, Me), 4.56(s, 2H, CH$_2$Br), 7.39(dd, 6-H), 7.98(dd, 5-H), 7.85(dd, 8-H), (J$_{5,6}$ 8.1, J$_{6,8}$ 1.5, J$_{5,8}$ 0.5)	60
6-Br, 3-CH$_2$, Br, 2-CH$_3$	2.59(s, Me), 4.56(s, 2H, CH$_2$Br), 7.45(dd, 7-H), 7.58(dd, 8-H), 7.94(dd, 5-H), (J$_{7,8}$ 8.2, J$_{5,7}$ 1.5, J$_{5,8}$ 0.6)	60
6-COCH$_3$, 2, 3-(CH$_3$)$_2$	2.24(s, 2 x Me), 2.62(s, Ac), 7.71(dd, 8-H), 7.94(dd, 7-H), 8.43(dd, 5-H), (J$_{7,8}$ 8.2, J$_{5,7}$ 1.4, J$_{5,8}$ 0.5)	60
2-Br, 3-CHO	10.03(CHO)	60
3-CHO	9.96(s, CHO), 8.18(s, 2-H)	60

TABLE 8 (Contd.)

Substituents	Chemical Shift δ (ppm), Multiplicity, Coupling Constants J (Hz)	Ref.
2-Br	7.3(s, 1H, 3-H)	60
2-CN	7.8(s, 1H, 3-H)	60
2, 6-Br$_2$	7.28(s, 3-H), 7.44(dd, 7-H), ($J_{7,8}$ 8.5, $J_{5,7}$ 1.6 Hz), 7.56(dd, 8-H), ($J_{5,8}$ 0.5), 7.93(dd, 5-H)	61
2-Acetyl	2.57(s, 3H, COMe), 7.87(s, 3-H)	61
2-CHO	10.04(s, CHO)	61
2-NO$_2$	8.16(s, 3-H)	61
2-Acetamido	2.15(s, COMe)	61
2-CH$_2$OH)	4.88(s, 2H, CH$_2$), 2.15(s, OH)	61

a = CDCl$_3$

Heating a mixture of 5-azidobenzo(b)thiophene, polyphosphoric acid and acetic acid at 135°C resulted in the formation of thienobenzo(b)oxazole, the structure of which was deduced from its n.m.r. spectrum.[49] Thus 2-methylthieno[2, 3-g]benzoxazole (XIX) showed two overlapping AB system ($J_{4,5}$ = 9.0, $J_{7,8}$ = 5.0 Hz) which agree with those obtained before for the 6,7(8.0-9.0 Hz) and 2,3-couplings (5.0-6.0 Hz) in benzo(b)thiophene systems.[18] The assignment of the low field AB quartet in the spectrum to the 4- and 5-protons followed from the coupling constants and from the collapse of the high field AB quartet to a singlet on substitution of the thiophene ring by an ester function (i.e.

XIX , R_1 = R_2 = H
XX , R_1 = COOEt , R_2 = H
XXI , R_1 = COOMe , R_2 = H
XXII, R_1 = H , R_2 = Me
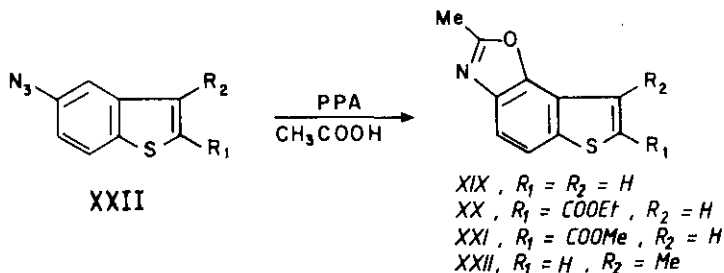
in compound XX and XXI), the 7-H signal of compound XXII was split by the adjacent methyl group.

Similar treatment of 5-azidobenzo(b)thiophene 1,1-dioxide resulted in the formation of 2-methylthieno-(3,2-f)benzoxazole-7,7-dioxide (XXIII). Its n.m.r. spectrum gave two pairs of doublets ($J_{4,8}$ = 0.5, $J_{5,6}$ = 7.0 Hz) in agreement with the values obtained for the 4,7(0.5-0.7 Hz) and 2,3-coupling (6.0-7.0 Hz) of benzo(b)thiophene 1,1-dioxides.[49]

XXIII
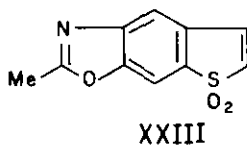
In a similar reaction, 6-azido-2,3-dibromobenzo(b)thiophene gave thieno[3,2-g]benzoxazole (XXIV). Its n.m.r. spectrum gave two singlets, one at δ 7.78 for the two aromatic protons, and one corresponding

XXIV

R_1 = R_2 = Br
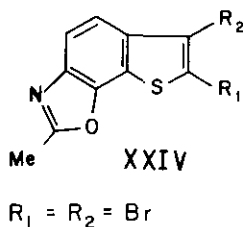
to the methyl group at δ 2.72. Addition of Eu(fod)$_3$ to a solution of XXIV in chloroform separated these signals and showed that they constituted an AB system with J 9.0 Hz, which is in agreement with the proposed angular structure.[50]

Cycloaddition of mesitonitrile oxide to 3-methylbenzo(b)thiophene-1-oxide in refluxing benzene led to the formation of two diastereoisomers XXVa-syn and XXVa-anti in a 1:1 ratio.[51] The n.m.r. assignments of the adduct XXVa-anti shows that the chemical shift of H_{3a}, eclipsed with the S-O bond, is situated at higher field (δ 4.78). In the second diastereoisomer XXVa-syn, the chemical shift of H_{3a} is at lower field (δ 5.15; $\Delta\delta$ = 0.37 ppm).


XXVa-syn , XXVa-anti
XXVe-syn , XXVe-anti

XXVI
XXVIa , R_2 = H , R_3 = CH_3
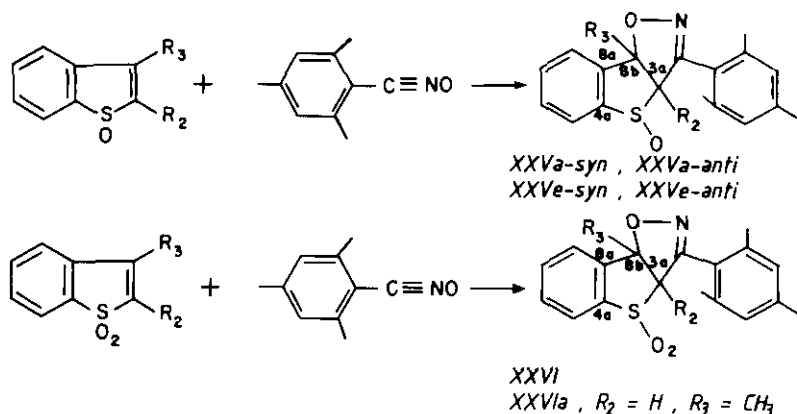
Heating a mixture of mesitonitrile oxide and benzo(b)thiophene-1,1-dioxide in refluxing benzene resulted in the formation of a single adduct XXVI.[51] The n.m.r. spectrum of XXVI shows two doublet signals (J = 9.5 Hz) at δ 5.37(1H) and 6.46(1H). Comparing this with the n.m.r. spectrum of XXVIa, the signal at higher field is assigned to H_{3a}, located at the α-position with respect to the sulphone group. In adduct XXVI the coupling constant ($J_{3a, 8b}$ = 9.5 Hz) of H_{3a} and H_{8b} located at the junction of the heterocycle is in agreement with a dihedral angle of 10°.

Irradiation of a solution of oxadiazole and benzo(b)thiophene in benzene afforded 3-benzoyl-benzo(b)thiophene (XXVII), benzoylhydrazone (XXVIII) and 1:1 cyclo-adduct (XXIX). Reduction of XXIX with sodium borohydride afforded a dihydro compound (XXX),[52] the n.m.r. spectrum of which exhibited methane proton signals at δ 4.67 (H_a, t, J = 8Hz), 6.23 (H_b, d, J = 28 Hz) and 6.32 (H_c, d, J = 8Hz), besides aromatic and NH proton signals. In the n.m.r. spectrum of XXIX-d_1 prepared from XXIX by reduction with sodium borohydride-d_4, the doublet at δ 6.32 does not appear. The two doublets, J(8Hz) are displayed at δ 4.67 and 6.25.
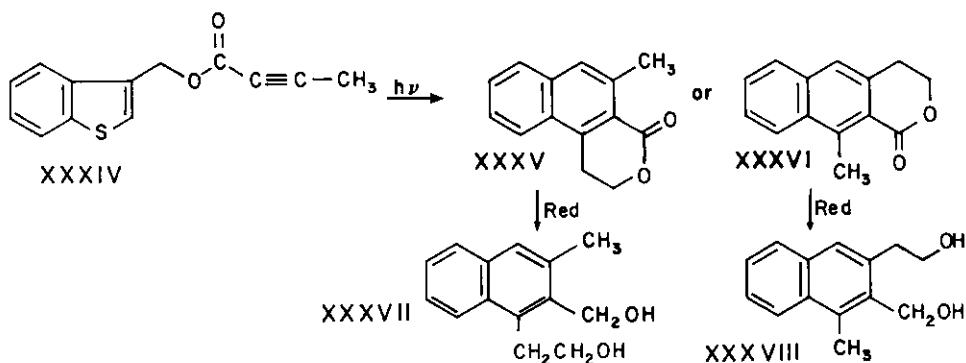

XXVII

XXVIII

XXX

XXIX
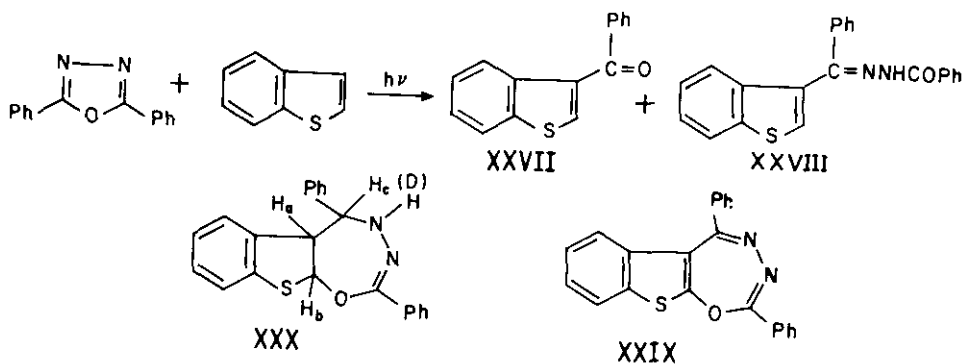
Irradiation of XXXI for 8 hr resulted in the formation of two monomeric photoadducts XXXII and
XXXIII.[53] N.m.r. of XXXIII revealed among others, an alkylic quartet (1H) at $\hat{\delta}$ 6.10 weakly coupled
(J = 1.6 Hz) with a methyl doublet (3H) at δ 1.86 and two multiplets centered at δ 2.28(2H) and
4.54 (2H), whereas the spectrum of XXXII gave a methyl doublet (3H) at δ 2.03, weakly coupled
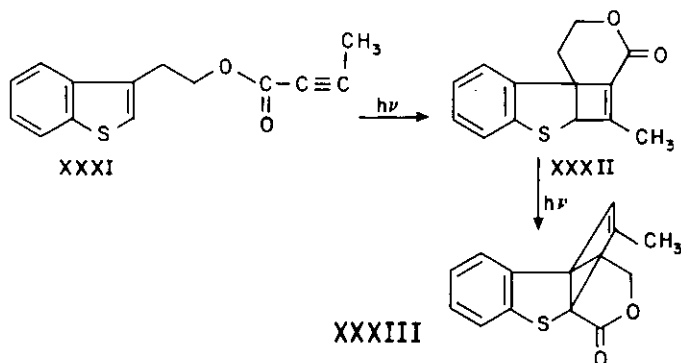
(J 1.2 Hz) with a methine doublet (1H) at δ 4.42.

On the other hand, 2-(2-benzothienyl)ethyl-but-2-ynoate (XXXIV) when irradiated in benzene in presence
of acetophenone for 23 hr gave only one product (XXXV),[53] the n.m.r. of which gave two-proton trip-
lets at δ 3.16 and 4.49, a deshielded methyl singlet at δ 8.23. The data are consistent with either
of the two naphthopyranone XXXV and XXXVI. Reduction with lithium aluminium hydride gave a diol
XXXVII and XXXVIII, the n.m.r. of which gave an absorption of an upfield methyl group at δ 2.47 with
an aromatic fine structure pattern in good agreement with 1,2,3-trisubstituted naphthalene. From a
relatively low chemical value of δ 2.74, it is most likely that XXXVIII is isolated naphthalene rather

than XXXVII, since β -methylnaphthalenes (δ CH$_3$ ~2.3-2.5) absorb about 0.2-0.3 ppm at higher field
than α-methylnaphthalenes.[54].
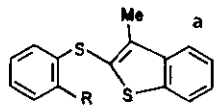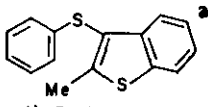
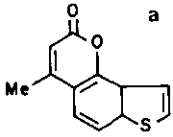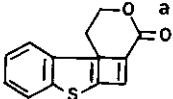The results are summarised in Table 9.

TABLE 9
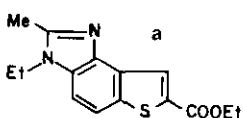
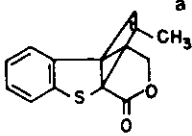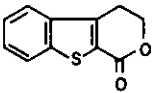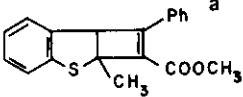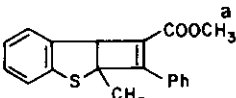| Compound	Chemical Shift δ (ppm), Multiplicity, Coupling Constant J(Hz)	Ref.
4-Azidobenzo(b)thiophene	7.45(6.65(m, aromatic H)	49
5-Azidobenzo(b)thiophene	7.10(d, 2-H), 7.37(d, 3-H), 7.31(d, 4-H), 6.88 and 6.68 (d, 6-H and 7-H), ($J_{4,6}$ 2.0, $J_{6,7}$ 9.0, $J_{2,3}$ 5.5)	49
Ethyl-5-azidobenzo(b)- thiophene-2-carboxylate	8.04(2-H), 7.55(d, 4-H), 7.17 and 7.89(d, 6-H and 7-H), ($J_{4,6}$ 2.0, $J_{6,7}$ 8.5), 4.56(q, J 7.0, CH_2), 1.43(t, J 7.0, CH_3)	49
Methyl-5-azidobenzo(b)- thiophene-2-carboxylate	7.96(3-H), 7.48(d, 4-H), 7.19 and 7.73(d, 6, 7-H), ($J_{4,6}$ 2.0, $J_{6,7}$ 9.0), 6.0(Me)	49
5-Azidobenzo(b)thiophene- 1,1-dioxide[d]	7.70-6.80(m)	49
3-Azidobenzo(b)thiophene- 1,1-dioxide	6.45(2-H), 7.85-7.50(m, 4, 5, 6, 7-H)	49
	8.72(1H, s, 8-H), 7.59 and 7.38(2H, d, 4-H and 5-H), ($J_{4,5}$ 7.0), 4.34(2H, q, J 7.0, CH_3), 4.22(2H, q, J 7.0, CH_2), 2.65(3H, s, 2-CH_3), 1.40(1.40(3H, t, J 7.0, CH_3), 1.38(3H, t, J 7.0, CH_3)	59
i) R = N₃ ii) R = aminophenyl	2.33(s, Me), 6.91-8.22(m, aromatic) 2.39(s, Me), 4.08(br, s, NH_2), 6.47-7.55(m, aromatic)	58
i) R = N₃ ii) R = aminophenyl	2.53(s, Me), 6.47-7.67(m, aromatic) 2.70(s, Me), 4.12(br, s, NH_2), 6.5-8.0(m, aromatic)	
	2.53(d, Me), 6.36(q, 3-H), 7.45(dd, 5-H), 7.72(dd, 6-H), 7.75(dd, 9-H), ($J_{5,6}$ 8.1, $J_{8,9}$ 5.9, $J_{3,Me}$ 0.8, $J_{6,9}$ 0.75, $J_{5,8}$ 0.45)	67
	1.86(d, 3H, CH_3, J 1.6), 2.17-2.38(m, 2H, CH_2), 4.43-4.64(m, 2H, CH_2), 6.10(q, 1H, H-aryl, J 1.6), 7.19(br, s, 4H, Ar)	67

TABLE 9 (Contd.)
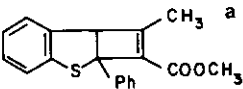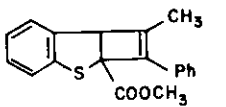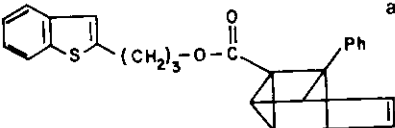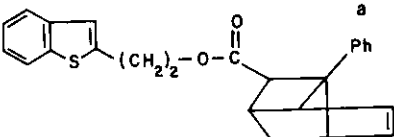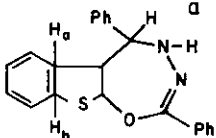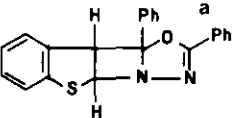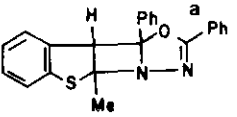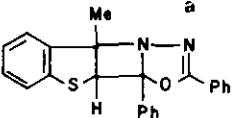
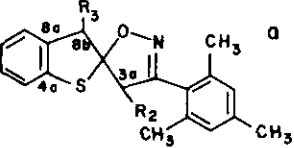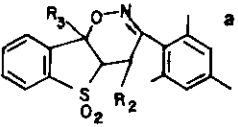| Compound	Chemical Shift δ (ppm), Multiplicity, Coupling Constant J(Hz)	Ref.
	2.03(d, 3H, CH$_3$, J 1.2), 2.42-2.63(m, 2H, CH$_2$), 4.40-4.88 (m, 2H, CH$_2$), 4.42(d, 1H, methine, J = 1.2 Hz), 7.12(br, s, 4H, Ar)	53
	3.20(t, 2H, CH$_2$), 4.76(t, 2H, CH$_2$), 7.40-8.19(m, 4H, Ar)	53
	1.90(s, 3H, CH$_3$), 3.87(s, 3H, COCH$_3$), 4.65(s, 1H, H$_5$ methine)	53
	1.94(s, 3H, CH$_3$), 3.84(s, 3H, COOCH$_3$), 4.42(s, 1H, H$_5$ methine)	53
	2.10(d, 3H, CH$_3$, J 1.4), 3.80(s, COOCH$_3$), 4.32(q, 1H, H$_5$ methine, J 1.2), 1.10-7.75(m, 9H, Ar)	53
	2.07(d, 3H, CH$_3$, J = 1.4 Hz), 3.78(s, 3H, COOCH$_3$), 4.78(q, 1H, H$_5$ methine, J 1.2)	53
	1.90(m, 2H, CH$_2$), 2.75(t, 2H, CH$_2$), 2.98(t, 2H, H$_2$ and H$_3$), 3.92(m, 2H, H$_1$ and H$_6$), 4.12(t, 2H, CH$_2$), 6.12(t, 2H, H$_7$ and H$_8$) 6.93(br s, 1H, H$_3$), 7.29-7.95(m, 9H, Ar), 7.28(s, 5H, Ph)	53
	3.03(t, 2H, H$_2$ and H$_3$), 3.11(m 2H, H$_1$ and H$_6$), 4.46(t, 2H, H$_7$ and H$_8$), 6.93(br s, 1H, H$_3$), 7.15-7.91(m, 9H, Ar), 7.25(s, 5H, Ph)	53
	4.67(1H, t, CH J 8.0), 6.23, 6.32(each 1H, d, CH, J 8), 6.5-7.8(14H, m, aromatic), 8.0(1H, br, NH)	52

TABLE 9 (Contd.)

Compound	Chemical Shift δ (ppm), Multiplicity, Coupling Constant J(Hz)	Ref.

4.85, 6.97(each 1H d, → CH, J 2.5 Hz), 7.1-8.0(14H, m, aromatic) — 52

2.04(3H, s, CH$_3$), 4.64(1H, s, → CH), 7.0-8.4(14H, m, aromatic) — 52

1.07(3H, s, CH$_3$), 6.87(1H, s, → CH), 7.0-8.1(14H, m, aromatic) — 52

1.95(s, CH$_3$), 5.15(s, 1H), 2.38(s, ortho-CH$_3$, 2.28(s, para-CH$_3$) — 52

2.15(CH$_3$), 4.78(s, 1H), 2.15(s, ortho-CH$_3$), 2.31(s, para-CH$_3$) — 52

5.23(s, 1H), 2.19(s, ortho-CH$_3$), 2.25(s, para-CH$_3$) — 52

4.97(s, 1H), 2.24(s, ortho-CH$_3$), 2.28(s, para-CH$_3$) — 52

syn, $R_3 = CH_3$, $R_2 = H$
anti, $R_3 = CH_3$, $R_2 = H$

syn, $R_3 = C_6H_5$, $R_2 = H$
anti, $R_3 = C_6H_5$, $R_2 = H$

6.4(d, H, J 9.5 Hz), 5.37(d, H, J 9.5), — 51

2.07(s, CH$_3$), 4.93(s, 1H), 2.20(s, ortho-CH$_3$), 2.90(s, p-CH$_3$),

5.00(s, 1H), 1.45(s, CH$_3$), 2.06-2.40(ortho-CH$_3$), 2.28(p-CH$_3$),

5.14(s, 1H), 2.29(s, ortho-CH$_3$), 2.39(s, p-CH$_3$),

5.78(s, 1H), 2.21(s, ortho-CH$_3$), 2.28(s, p-CH$_3$), 1.56-1.70(m, piperidine H)

i), $R_2 = R_3 = H$
ii), $R_2 = H$, $R_3 = CH_3$
iii), $R_2 = CH_3$, $R_3 = H$
iV), $R_2 = H$, $R_3 = C_6H_5$
V), $R_2 = H$, $R_3 = $

a = CDCl$_3$, b = CCl$_4$

Reaction of 2, 3, 5-trimethylbenzo(b)thiophene with isopropyl iodide and silver tetrafluoroborate resulted in the formation of two products XXXIX and XL, which were identified by their n.m.r. spectra.[55]
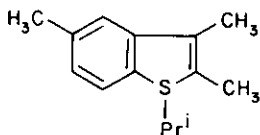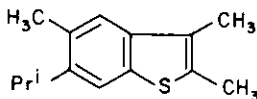
The 5-methyl group gave separate singlets at δ 2.51 and 2.49 and similarity of their intensities indicated a 1:1 mixture. The 2- and 3-methyl groups appeared at δ 2.45 and 2.35 respectively. The methyl groups of the isopropyl groups were non-equivalent and gave rise to four pairs of doublets at δ 1.30-1.10. The methine proton gave a quintuplet at δ 4.58. The 6-isopropyl group of XXXV showed as a six-proton doublet at δ 1.50 and a one-proton septuplet at δ 3.14. A low field sharp singlet at δ 7.82 confirmed the 6-substitution. The 7-proton of XXXIV gave a doublet at δ 7.90 (J 8Hz).

Comparison of the chemical shifts of the protons of the 1-alkylbenzo(b)thiophenium salts with those of the parent compounds, the results obtained showed (Table 10) that for the benzo(b)thiophenium salts, the general trend is 3H > 7-H > 6-H > 4-H > 2-H and for the dibenzo(b,d)thiophenium salts (1-5) 3-H > 4-H > 2-H > 1-H. The large downfield shift of the 3-proton [cf. (XLI)] relative to the 2-proton [cf. (XLII)] is consistent with the view that (XIII) is a resonance contributor of little importance.
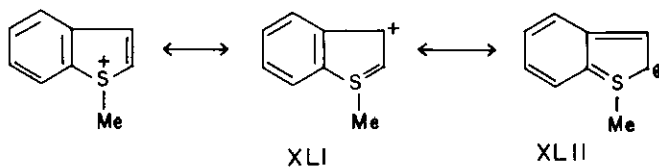
The 7-proton signal for the benzo(b)thiophenium salts was always observed as a low field doublet and similar large downfield shift relative to the parent benzo(b)thiophene for both the 6- and 7-protons show that there must be considerable interaction between the positively charged sulphur atom and the carbocyclic ring. The downfield shift for 5-proton was greater than that of the 4-proton.[55]

In case of the cis- and trans-2-styrylbenzo(b)thiophenium salt, the 1-methyl and 7-proton resonances in the cis-isomer were in the range of 0.3-0.4 and 0.14-0.22 ppm to high field of those of the trans-isomers. This is consistent with the non-planar conformation taken up by the cis-isomer and shielding by the phenyl ring. S-methylation leads to little change in the chemical shifts of the styryl proton adjacent to the charged ring is shifted to 0.6 ppm downfield, which must be due to the preferred steric arrangement of the cis-isomer, resulting in the styryl proton lying in the deshielding zone of the sulphur atom.[55]

The results are summarised in Table 10.

TABLE 10

$$\overset{\displaystyle\text{(structure)}}{\text{BF}_4^-}$$
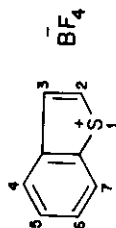
NMR DATA OF THE ALKYL BENZO(b)THIOPHENIUM SALTS

Substituents	Chemical Shifts δ (ppm)[a], Multiplicity, Coupling Constant J (Hz)	
	S-Alkyl	Other Protons
1-CH$_3$ᵐ	3.37	2-H, 7.53, $J_{2,3}$ 5.7; 3-H, 7.92; 4,5,6-H, 8.0-7.6, m, $J_{5,7}$ 2.3; 7-H, 8.3, q, $J_{6,7}$ 6.8
1-C$_2$H$_5$ᵐ	CH$_2$, 4.07[a], q; Me J 7, 1.02, t;	2-H, 7.37, d, $J_{2,3}$ 5.7; 3-H, 7.93, d, 4,5,6-H, 8.0-7.6, m; 7-H, 8.25, q, $J_{6,7}$ 6.8
1,2-(CH$_3$)$_2$ᵐ	3.35	2-Me, 2.60, $J_{2,3}$ <u>ca</u> 1; 3-H, 7.44[b]; 4,5,6-H, 7.5-7.9; 7-H, 8.25, d, $J_{6,7}$ 7.1
1-C$_2$H$_5$, 2-CH$_3$ᵐ	CH$_2$, 3.7-4.3, m, Me, 0.97, t;	2-Me, 2.53; 3-H, 7.49, d, $J_{2,3}$ <u>ca</u> 1[c]; 4,5,6-H, 7.55-7.85, m; 7-H, 8.15, d[b], $J_{6,7}$ 7.1
1,3-(CH$_3$)$_2$ᵐ	3.35	2-H, 7.21, d, $J_{2,3}$ 1.2[d]; 3-Me, 2.52; 4,5,6-H, 7.6-7.95, m; 7-H, 3.34, q, $J_{5,7}$ 1.8
1-C$_2$H$_5$, 3-CH$_3$ᵃ	CH$_2$, 4.10, q; Me, 0.99, t; J 7	2-H, 7.12, d, $J_{2,3}$ 1.0[d]; 3-Me, 2.54; 4,5,6-H, 7.65-7.95, m; 7-H, 8.38, d[b], $J_{6,7}$ 7.4
1,2,3-(CH$_3$)$_3$ᵃ	4.30	2-Me, 2.49ᵗ; 3-Me, 2.36ᵗ; 4,5,6-H, 7.5-7.9, m; 7-H, 8.26, d, $J_{6,7}$ 7.4
1-C$_2$H$_5$, 2,3,4-(CH$_3$)$_2$	CH$_2$, 3.7-4.4, m; Me, 0.94, t	2-Me, 2.49ᵗ; 3-Me, 2.40ᵗ; 4,5,6-H, 7.5-7.9, m; 7-H, 8.23, d, $J_{6,7}$ 7.4

TABLE 10 (Contd.)

Chemical Shifts δ (ppm)[a], Multiplicity, Coupling Constant J(Hz)

| Substituents	s-Alkyl	Other Protons
$1,2,3,5$-$(CH_3)_4$[m]	3.38	2-Me, 2.47[t]; 3-Me, 3.35[t]; 4-H, 7.54[b]; 5-Me, 2.51; 6-H, 7.45[b], d, $J_{6,7}$ 8.0; 7-H, 8.12, d
1-C_2H_5, $2,3,5$-$(CH_3)_3$[a]	CH_2, 3.6-4.40, m; Me, 0.93, t	2-Me, 2.47[t]; 3-Me, 2.37[t]; 4-H, 7.50; 5-Me, 2.52; 6-H, 7.44, d, $J_{6,7}$ 8.0; 7-H, 8.10, d
2-Br, 1-C_2H_5[m]	CH_2, 3.8-4.5, m; Me, 1.04, t	3-H, 8.05; 4,5,6-H, 7.7-8.0, m; 7-H, 8.37, d[b], $J_{6,7}$ 7;
3-Br, 1-CH_3[m]	3.38	2-H, 7.56; 4,5,6-H, 7.7-8.1, m, $J_{5,7}$ 1.8; 7-H, 8.27, q[b], $J_{6,7}$ 7.4
3-Br, 1-C_2H_5[m]	CH_2, 4.0-4.4, m; Me, 1.03, t	2-H, 7.56; 4,5,6-H, 7.7-8.1, m, $J_{5,7}$ 1.8; 7-H, 8.37, q, $J_{6,7}$ 7.4
$2,3$-$(Br)_2$, 1-CH_3[n]	3.40	4,5,6-H, 7.8-8.05, m, $J_{5,7}$ 2.0; 7-H, 8.29, q, $J_{6,7}$ 7.4
5-Cl, 1-CH_3[n]	3.27	2-H, 7.47, d, $J_{2,3}$ 5.4; 3-H, 7.91, d; 4-H, 8.03, d, $J_{4,6}$ 2.0; 6-H, 7.75, d, $J_{6,7}$ 8.3; 7-H, 8.23, d
5-Cl, 1-C_2H_5[m]	CH_2, 4.13, 1, J 7.1; Me, 1.03, t, J 7.1	2-H, 7.48, d, $J_{2,3}$ 5.4; 3-H, 7.90; 4-H, 7.95, d, $J_{4,6}$; 6-H, 7.73, q, $J_{6,7}$ 8.3; 7-H, 8.25, d
1-CH_3, 2-CH_2CH_2Ph[m]	3.20	2-Ph-$\underline{CH_2}$-CH_2-, 2.75, s; 2-Ph-CH_2-$\underline{CH_2}$-, 3.0-3.15, m; 3-H, 7.42; 4,5,6-H, 7.5-7.8, m; 7-H, 8.22, d[b], $J_{6,7}$ 7.4
1-C_2H_5, 2-CH_2CH_2Ph[m]	CH_2, 3.5-4.3, m; Me, 0.90, t	2-Ph$CH_2$$\underline{CH_2}$-, 7.30, s; 2-Ph$\underline{CH_2}$$CH_2$, 3.15, s; 3-H, 7.51; 4,5,6-H, 7.55-7.85, m; 7-H, 8.15, d[b], $J_{6,7}$ 7.4
1-CH_3, trans-2-styryl[m]	3.36	ArH(2H), 7.5-7.7, m; ArH(3H), 7.2-7.5, m; 7.00, d[g]; 7.33, d[g]; J 16.0[g]; 3-H, 7.62, s; 4,5,6-H, 7.55-7.9, m; 7-H, 8.26, d, $J_{6,7}$ 7.4
1-C_2H_5, trans-2-styryl[a]	CH_2, 3.6-4.4, m; Me, 0.91, t, J 7.1	ArH(2H), 7.45-7.6, m; ArH(3H), 7.2-7.5, m; 7.00, d[g]; 7.37, d[g]; J 16.0[g]; 3,4,5,6-H, 7.45-7.90, m; 7-H, 8.15, d[b], $J_{6,7}$ 7.4

TABLE 10 (Contd.)

Substituents	Chemical Shift δ (ppm)[a], Multiplicity, Coupling Constant J(Hz)	
	S-Alkyl	Other Protons
1-C$_2$H$_5$, trans-2-(4-Cl-Styryl)	CH$_2$, 3.8-4.3, m;	ArH(2H), 7.5-7.7, m; ArH(3H), 7.2-7.3, m; 7.01, d[g]; 7.36, d[g];
5-Cl, 1-CH$_3$, trans-2-styryl[n]	Me, 0.92, t, J 7.1	J 15.6[g]; 3-H, 7.77, s[t]; 4,5,6-H), 7.5-7.8, m; 7-H, 8.15, d, J$_{6,7}$ 7.4
	3.32	ArH(2H), 7.6-7.8, m; ArH(3H), 7.35-7.55, m; 7.06, d[g]; 7.38, d[g];
		7-H, 8.20, d, J$_{4,6}$ 2.0; 6-H, 7.7;
		7-H, 8.20, d, J$_{6,7}$ 8.2
5-Cl, 1-C$_2$H$_5$, trans-2-styryl[m]	CH$_2$, 3.7-4.3, m;	ArH(2H), 7.5-7.7, m; ArH(3H), 7.3-7.5, m; 7.08, d[g]; 7.38[t,g] d;
	Me, 0.96, t, J 7.1	J 16.0[g]; 3-H, 7.67, 4-H, 7.80, d, J$_{4,6}$ 2.0; 6-H, 7.62, m[e];
		7-H, 8.17, d, J$_{6,7}$ 8.0
1-CH$_2$-I, 2,3-(CH$_3$)$_2$[p]	CH$_2$, 5.22, d; 5.41, d;	2,3-Me, obscured by solvent; 4,5,6-H, 7.6-8.0, m;
	J 13.0	7-H, 8.10, d[b], J$_{6,7}$ 7.8
1-CH$_2$-I, 2,3-(CH$_3$)$_2$[a]	obscured by solvent	2,3-Me, 2.37; 4,5,6-H, 7.6-8.0, m; 7-H, 8.20, d[b]; J$_{6,7}$ 8.0,
1-CH$_2$CH$_2$Br, 2,3,5-(CH$_3$)$_3$[a]	CH$_2$, 3.85-4.5, m;	2-Me, 2.44[t]; 3-Me, 2.35[t], 4-H, 7.68[b]; 5-Me, 2.53; 6-H, 7.53, d,
	CH$_2$, 3.0-3.6, m	J$_{6,7}$ 8.0; 7-H, 8.03, d
1-CH$_2$CH$_2$Ph, 2,3,5-(CH$_3$)$_3$[p]	ArH(5H), 7.0-7.2, m;	2-Me, 2.34[t]; 3-Me, 2.29[t], 4-H, 7.48; 5-Me, 2.51;
	CH$_2$, 3.85-4.5, m;	6-H, 7.40, d, J$_{6,7}$ 8.0; 7-H, 7.96, d
	CH$_2$, 2.64, t	

a. CDCl$_3$; b. some further splitting; c. coupling constant between 3-proton and 2-CH$_3$; d. coupling constant between 2-H and 3-CH$_3$;

e. partially concealed by other resonances; f. assignment uncertain; g. vinyl proton; m. CH$_2$Cl$_2$; n. CD$_3$CN; p. CH$_3$CN

The n.m.r. spectra of several benzo(b)thiophene-1,1-dioxides show the following features. (a) 2-H and 4-H are consistently shielded. (b) 5-H and 6-H are consistently deshielded. (c) 3-H is little affected and the changes in 7-H are small and of variable sign.[18] The loss of aromaticity of the thiophene ring on oxidation of the sulphur atom leads to a more localised 2,3-double bond and a consequent increase in $J_{2,3}$, $J_{2,3}$ and $J_{2,3}$, $J_{2,6}$ is no longer observed, since the conjugated pathway (VIII) over which this coupling operates is partially removed by oxidation of the sulphur atom. The overall upfield shift of 2-H has been attributed to the ring current and the anisotropy effect, whereas the downfield shift of 4-H and 6-H to the dipole field effect. The small effect on 7-H has been attributed to the opposing factors, i.e. anisotropy and dipole field effects.[18]

In the reaction of 3-(α-chloroethyl)benzo(b)thiophene-1,1-dioxide (XLIV) with piperidine the product (XLIII) showed in addition to four phenyl protons and ten piperidine protons a methyl doublet at δ 1.49 (J = 7.4 cps), a one-proton quartet at δ 4.11 (J = 7.4 cps) and a one-proton singlet at δ 6.67. On the other hand treatment of 3-(α-chloro-α-methylethyl)benzo(b)thiophene (XLIV) in piperidine and
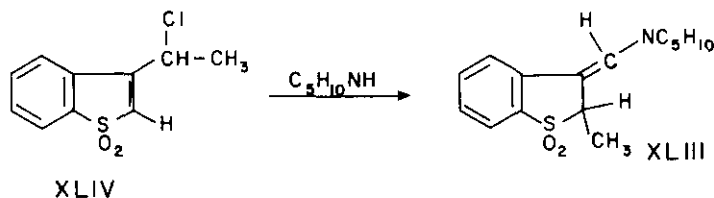
benzene gave a high yield of an enamine (XLVI). Its n.m.r. spectrum revealed four aromatic protons, ten piperidine protons and a dimethyl singlet at (δ 1.52, 6H). This spectrum differentiates it from
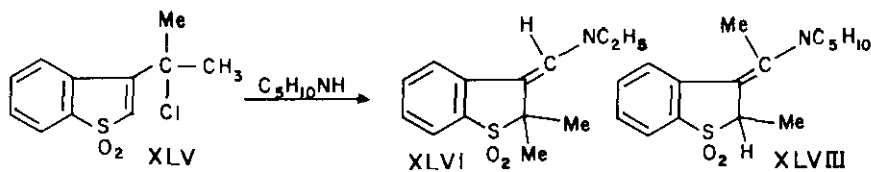
the other possible compound (XLVI), having two distinct methyl groups, should give a doublet for one of the methyl. Further proof comes from the hydrolysis of the enamine which gave a carbonyl compound (XLVIII), the n.m.r. spectrum of which revealed an aldehydic hydrogen at δ 9.72 and a methinyl hydrogen as a doublet at δ 3.87 (J 3.7 cps), in place of the signals for the vinyl and piperidine proton.[88]
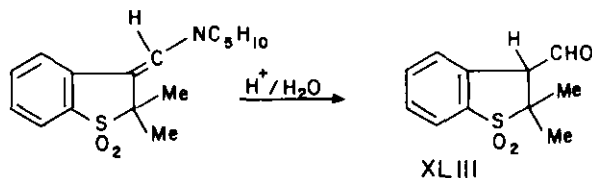
The chemical shifts of the protons and coupling constants of several 1,1-dioxides are listed in Table 11.

TABLE 11

CHEMICAL SHIFTS IN SUBSTITUTED BENZO(b)THIOPHENE, 1,1-DIOXIDE

Substituent	Chemical Shift δ(ppm), Multiplicity, Coupling Constant J (cps)	Ref.
5-CH$_3$	2-H, 6.65, J$_{2,3}$ 6.7; 3-H, 7.15, J$_{3,7}$ 0.8; 4-H, 7.12; 6-H, 7.26, J$_{6,7}$ 7.5; 7-H, 7.54	18
5-Br	2-H, 6.75, J$_{2,3}$ 6.7; 3-H, 7.17, J$_{3,7}$ 0.7; 4-H, 7.46, J$_{4,6}$ 2.0, J$_{4,7}$ 0.6; 6-H, 7.62, J$_{6,7}$ 8.4; 7-H, 7.53	18
2-Br	3-H, 7.33, s	88
3-Br	2-H, 7.00, s	88
2-CH$_3$	2-Me, 2.17, d, J 1.7; 3-H, 6.85, q, 1.7	88
3-CH$_3$	2-H, 6.58, q, J 1.5; 3-Me, 2.25, d, J 1.5	88
3-C$_2$H$_5$	2-H, 6.48, t, J 1.5; -CH$_2$CH$_3$, 2.63, q, J 7.5, J 1.5[b]; -CH$_2$CH$_3$, 1.28, t, J 7.5	88
3-CH$_2$Cl	2-H, 6.67, t, J 1.5; CH$_2$Cl, 4.47, d, J 1.5	38
3-CH(OH)CH$_3$	2-H, 6.73, d, J 1.4; 3-CH(OH)CH$_3$, 4.98; 3-CH(OH)CH$_3$, 1.52, d, J 7.0; 3-CH(OH)CH$_3$, 3.46, d, J 4.7	88
3-CHClCH$_3$	2-H, 6.72, d, J 1.3; 3-CHClCH$_3$, 5.02, q, J 7.0, J 1.3[b]; 3-CHClCH$_3$, 1.82, d, J 7.0	88
2-CHClCH$_3$	3-H, 7.25, d, J 1.5; 2-CHClCH$_3$, 5.10, q, J 6.9, J 1.5[b]; 2-CHClCH$_3$, 1.98, d, J 6.9	88
3-CH(NC$_5$H$_{10}$)CH$_3$	2-H, 6.55, s; 3-CH(piperidine)CH$_3$, 3.70, q, J 6.3; 3-CH(piperidine)CH$_3$, 1.28, d, J 6.3; piperidine protons (α, 2.48; β and γ, 1.46)	88
2-CH(NC$_5$H$_{10}$)CH$_3$	3-H, 7.03; 2-CH(piperidine)CH$_3$, 3.87, q, J 6.8, J 1.1[b]; 2-CH(piperidine)CH$_3$, 1.42, d, J 6.8; piperidine protons (α, 2.55; β and γ, 1.51)	88
3-CH$_2$O(p-anisoyl)	2-H, 6.75, t, J 2.0; 3-CH$_2$-O(p-anisoyl), 5.35, d, J 2.0; -OCH$_3$, 3.85, s.	88
3-CH$_2$O(mesitoyl)	2-H, 6.77, t, J 1.7; 3-CH$_2$-O(mesitoyl), 5.38, d, J 1.7; O, P-CH$_3$, 2.29, s	88
3-CH$_2$OCH$_2$CH$_3$	2-H, 6.65, t, J 1.5; 3-CH$_2$OCH$_2$CH$_3$, 4.48, d, J 1.5; 3-CH$_2$OCH$_2$CH$_3$, 3.60, q, J 7.0; 3-CH$_2$O-CH$_2$-CH$_3$, 1.23, t, J 7.0	88
3-CH$_2$NC$_5$H$_{10}$	2-H, 6.84, t, J 1.5; 3-CH$_2$NC$_5$H$_{10}$, 3.55, d, J 1.5; piperidine protons, (α, 2.5; β and γ, 1.5)	88

TABLE 11 (Contd.)

CHEMICAL SHIFTS IN SUBSTITUTED BENZO(b)THIOPHENE, 1,1-DIOXIDE

Substituents	Chemical Shifts δ (ppm), Multiplicity, Coupling Constant J (cps)	Ref.
2,3-$(CH_3)_2$	2,3-CH_3, 2.12, s	88
2-Br, 3-CH_3	3-Me, 2.25, s	88
2-Br, 3-C_2H_5	CH_2, 2.72, q, J 7.5; CH_3, 1.23, t, J 7.5	88
2-C_2H_5, 3-Br	CH_2, 2.73, q, J 8.0; CH_3, 1.38, t, J 8.0	88
2-CH_3, 3-CH_2Cl	2-CH_3, 2.20, s; 3-CH_2, 4.48, s	88
2-CH_2Cl, 3-CH_3	2-$\underline{CH}_2$, 4.55, s; 3-CH_3, 2.28, s	88
2-CH_3, 3-$CH_2NC_5H_{10}$	2-CH_3, 2.20, s; 3-$\underline{CH}_2$(piperidine), 4.43, s; piperidine protons (α, 2.45; β and γ, 1.50)	88
2-$CH_2NC_5H_{10}$, 3-CH_3	2-$\underline{CH}_2$(piperidine), 3.49, s; 3-CH_3, 2.28, s; piperidine protons (α, 2.48, β and γ, 1.50)	88
3-CH_3, 5-F	2-H, 6.54, $J_{2,3}$ 1.5; 4-H, 7.09, $J_{4,6}$ 2.0, $J_{4,7}$ 0.5; 6-H, 7.19, $J_{6,7}$ 8.4; 7-H, 7.68	88
3-CH_3, 5-Cl	2-H, 6.51, $J_{2,3}$ 1.5; 4-H, 7.36, $J_{4,6}$ 1.7, $J_{4,7}$ 0.6; 6-H, 7.48, $J_{6,7}$ 8.0; 7-H, 7.61	88
3-CH_3, 5-Br	2-H, 6.49, $J_{2,3}$ 1.5; 4-H, 7.52, $J_{4,6}$ 1.7, $J_{4,7}$ 0.5; 6-H, 7.65, $J_{6,7}$ 8.1; 7-H, 7.55	88
3-CH_3, 5-I	2-H, 6.45, $J_{2,3}$ 1.5; 4-H, 7.72, $J_{4,6}$ 1.5, $J_{4,7}$ 0.5; 6-H, 7.87, $J_{6,7}$ 8.4; 7-H, 7.41	88
3-CH_3, 5-NO_2	2-H, 6.66, $J_{2,3}$ 1.6; 4-H, 8.23, $J_{4,6}$ 2.0, $J_{4,7}$ 0.6; 6-H, 8.43, $J_{6,7}$ 8.4; 7-H, 7.88	88
3-Br, 5-NO_2	2-H, 7.16; 4-H, 8.39, $J_{4,6}$ 2.0, $J_{4,7}$ 0.7; 6-H, 8.50, $J_{6,7}$ 8.3; 7-H, 7.92	88
2,3-$(CH_3)_2$, 5-Cl	4-H, 7.32, $J_{4,6}$ 1.8, $J_{4,7}$ 0.6; 6-H, 7.40, $J_{6,7}$ 8.1; 7-H, 7.62	88
2,3-$(CH_3)_2$, 5-Br	4-H, 7.48, $J_{4,6}$ 1.9, $J_{4,7}$ 0.3; 6-H, 7.58, $J_{6,7}$ 8.0; 7-H, 7.56	88

a. In deuteriochloroform; b. quartet of doublets.

The multiplicity is abbreviated thus: s. singlet, d. doublet, t. triplet, q. quartet

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