Effects of Lanthanide Shift Reagents on ^1H NMR Spectra of 1- (X-Benzo [b] Thienyl) Ethyl Acetate Derivatives

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Summary: The analysis of the high resolution spectrum of 1- (X-benzo [b] thienyl) ethyl acetate derivatives in several solvents is reported. It is noted that some spectra are deceptively simple. The coupling constants derived from different solvents are remarkably consistent. Also, it was shown that no appreciable differences in coupling constants derived before and after the addition of lanthanide shift reagents (LSR). Long-range coupling constants over five and four bonds were observed. A substantial downfield shift was observed at H_3 and H_4 arising from peri-interaction of the 3-H or 4-H and methine protons of ethylacetate group substituted at position 4 or 3 respectively. Lanthanide-induced shifts (LIS) are discussed for the title compounds. The shift reagent leads to spectroscopic differentiation of the different protons.

Introduction

The ^1H NMR spectra of many aromatic and heterocyclic compounds have been investigated in detail[1]. Most of the detailed investigation of bicyclic systems has been restricted to a refined study of the spectra of the parent compound and few of its simple derivatives, e.g., benzo [b] furan[2,3], indole[3] and quinoline[4/6].

The benzo [b] thiophene system has been studied by a number of workers[7,8]. The present work discuss the ^1H NMR spectra of some 1- (X-benzo [b] thienyl) ethylacetate, where X=2 to 7 positions. The substituent effects have been investigated in many solvents, e.g. chloroform-d, methanol-d_4, benzene-d_6, dimethyl sulphoxide-d_6 and acetone-d_6.

Our interest in the present results is threefold: firstly; influence of substituents on the chemical shifts of the ring protons, as a guide for structures elucidation of these series, with an attempt to extrapolate these studies to the NMR parameters in aromatic systems in general. Secondly; observation of long-range Spin-Spin and ring-side chain coupling lead to more confirmation concerning "straight zig-zag path"[9,10]. Thirdly; effects of lanthanide shift reagents[11,12] to simplify complex spectra to first order spectra which enabled reliable assignments of chemical shifts and coupling constants.[13]

Results and discussion

The influence of substituents on the chemical shifts of ring protons in benzenoid, polynuclear, and heteroaromatic systems has been the subject of a large nember of communications most of which have been summarized[1,14] or discussed in recent publications[2,7,15]. The chemical shift assignments relative to the parent heterocycle for benzo [b] thiophene and benzo [b] thienyl ethylacetate derivatives are listed in Tables 1 and 2.

Benzo [b] thiophene:

The chemical shifts for the benzo [b] thiophene protons are given in tables 1 and 2. The assignments for benzo [b] thiophene (1), are based on assignments in the literature[8] and were confirmed by substitution of ethylacetate group in positions 2 to 7 and using different solvents for ^1H NMR analyses.

Benzo [b] thiopenes:

The chemical shifts for the benzo [b] thiophene derivatives has been achieved based on their coupling mode and their behaviour in aromatic and non-aromatic solvents. Double irradiation and lanthanide shift reagents

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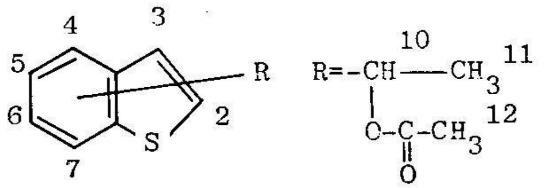
were used to simplify and evaluate molecular structure and coupling constants.



1-(X-benzo [b] thienyl) ethyl acetates:

The benzenoid protons, (X=2 or 3) Tables 1 and 2, are treated as a modified ABCD System, according to the method of Batterham et al[16] we found that ABCD systems can be best studied in certain substituted benzo [b] thiophenes where the AB System from the 2 and 3-protons is absent and where the substituent separates the two AB multiplets of the four-spin systems. Ideal example of this was observed in the 100-MHz spectra of 1-(3-benzo [b] thienyl) ethyl acetate in benzene (Fig.1). It was shown before that the peak patterns of the AB,C, and D groups in the condensed aromatic systems are characteristic for given values of δ AB and that the C and D multiplets are almost mirror images of each other. Indeed, Fig.1. shows that the downfield multiplets is due to H_4 and H_7 being mirror-images of each other (no long-range coupling between H_7 and H_3 due to the substituent at position 3), δ_4 and δ_7 are readily obtained. However, in chloroform and acetone solutions, δ_4 and δ_7 are well resolved, but the two multiplets are close and being mirror-images of each other. H_5 and H_6 are readily obtained. H_2 signal appears as a doublet with spin-spin

Table 1. Chemical Shifts of the Protons in Benzo [b] thiophene and 1-(X-benzo[b] thienyl) ethyl Acetate Derivatives 0.1M in Chloroform-d ($R = -\underset{\underset{OCOCH_3}{|}}{CH}CH_3$).

Compound	Substituent		H_2	H_3	H_4	H_5	H_6	H_7	H_{10}	H_{11}	H_{12}
1	None	δ	7.40	7.29	7.78	7.33	7.31	7.86	—	—	—
2	2–R	δ	—	7.23	7.68	7.29	7.27	7.76	6.20	1.67	2.07
		$\Delta\delta$	—	+6	+10	+4	+4	+10	—	—	—
3	3–R		7.39	—	7.84	7.34	7.30	7.80	6.31	1.68	2.07
			+1	—	–6	–1	+1	+6	—	—	—
4	4–R		7.46	7.54	—	7.37	7.29	7.81	6.34	1.64	2.07
			–6	–25	—	–4	+2	+5	—	—	—
5	5–R		7.38	7.24	7.72	—	7.24	7.80	6.00	1.56	2.04
			+2	+5	+6	—	+7	+6			
6	6–R		7.40	7.28	7.75	7.31	—	7.86	6.00	1.59	2.08
			–0.0	+1	+3	+2	—	0.0			
7	7–R		7.42	7.38	7.73	7.39	7.26	—	6.16	1.67	2.12
			–2	–9	+5	–6	+5				
8	1-phenyl-ethyl acetate			C_6H_5–	one peak	at	7.29	—	5.87	1.45	2.01
9	1-phenyl ethyl alcohol			C_6H_5–	one peak	at	7.34	–OH 1.85	4.89	1.49	1.85

$\Delta\delta = \delta$ Non – δ Subst. (Hz), (–) downfield Shif, (+) upfield Shift.

Table 2. Chemical Shifts of the Protons in Benzo [b] thiophene and 1-(X-benzo [b] thienyl) ethyl Acetate Derivatives in 0.1M of Different Solvents.

Compound	Substituent			H_2	H_3	H_4	H_5	H_6	H_7	H_{10}	H_{11}	H_{12}
1	None	A		7.58	7.39	7.85	7.35	7.33	7.93	—	—	—
		B		6.99	6.96	7.55	7.13	7.06	7.59	—	—	—
2	2–R	A	δ	—	7.36	7.80	7.38	7.33	7.88	6.19	1.65	2.05
			$\Delta\delta$	—	+3	+5	–3	0.0	+5	—	—	—
		B	δ	—	6.97	7.49	7.10	7.07	7.49	6.22	1.44	1.66
			$\Delta\delta$	—	–1	+6	+3	–1	+10	—	—	—
		C	δ	—	7.29	7.73	7.32	7.30	7.81	6.19	1.66	2.06
		D	δ	—	7.42	7.82	7.37	7.34	7.90	6.15	1.62	2.07
3	3–R	A	δ	7.63	—	7.94	7.43	7.38	7.85	6.31	1.69	2.09
			$\Delta\delta$	–5	—	–9	–8	–5	+8	—	—	—
		B	δ	6.98	—	7.78	7.17	7.09	7.54	6.32	1.43	1.65
			$\Delta\delta$	–1	—	–23	–4	–3	–5	—	—	—
4	4–R	A	δ	7.70	7.63	—	7.41	7.39	7.88	6.31	1.61	2.04
			$\Delta\delta$	–12	–24	—	–6	–6	+5	—	—	—
		B	δ	6.98	7.35	—	7.23	7.07	7.51	6.38	1.44	1.65
			$\Delta\delta$	+1	–39	—	–10	–1	+8	—	—	—
		e	δ	7.62	7.62	—	7.38	7.30	7.85	6.31	1.59	2.03
			$\Delta\delta$	–4	–23	—	–3	+3	+8	—	—	—
6	6–R	A	δ	7.63	7.40	7.85	7.39	—	7.97	6.01	1.56	2.04
			$\Delta\delta$	–5	–1	0	–4	—	–4	—	—	—
		B	δ	6.93	6.92	7.51	7.17	—	7.67	6.00	1.37	1.66
			$\Delta\delta$	+6	+4	+4	–4	—	–8	—	—	—
		D	δ	7.72	7.57	7.78	7.45	—	8.07	5.99	1.53	2.05
7	7–R	A	δ	7.65	7.45	7.81	7.38	7.38	—	6.12	1.63	2.07
			$\Delta\delta$	–7	–6	+4	–3	–5	—	—	—	—
		B	δ	7.00	6.95	7.49	7.17	7.10	—	6.25	1.50	1.73
			$\Delta\delta$	–1	+1	+6	–4	–4	—	—	—	—

A = Acetone-d_6, B = Benzene -d_6, C = methanol -d_4, D = Dimethylsulphoxide-d_6. e = 30% in acetone-d_6.

coupling to side ring chain proton, H_{10}, by 0.73 Hz and separated from the other protons (in acetone), and a reliable analysis for H_5 and H_6 can be determined due to the absence of the overlap of the H_2 signal.

In 1-(2-benzo [b] thienyl) ethyl acetate, δ_4 and δ_7 are readily obtained, the multiplets of H_7, differ from that of H_4 due to the long range coupling between H_7 and H_3. H_3 signal overlaps with H_5 and H_6 multiplets, however, the midpoint of H_3 can be determined by inspection, (strong doublet split of 0.73Hz due to the coupling with H_7 and H_3 or by double irradiation at H_7 which lead to the appearance of H_2 as a doublet due to the coupling with side chain H_{10} of 0.73 Hz). One of the tricky assignment is how to differentiate between H_4 and H_7. Substitution at position 2, makes H_7 readily identified, appearing downfield than H_4 with

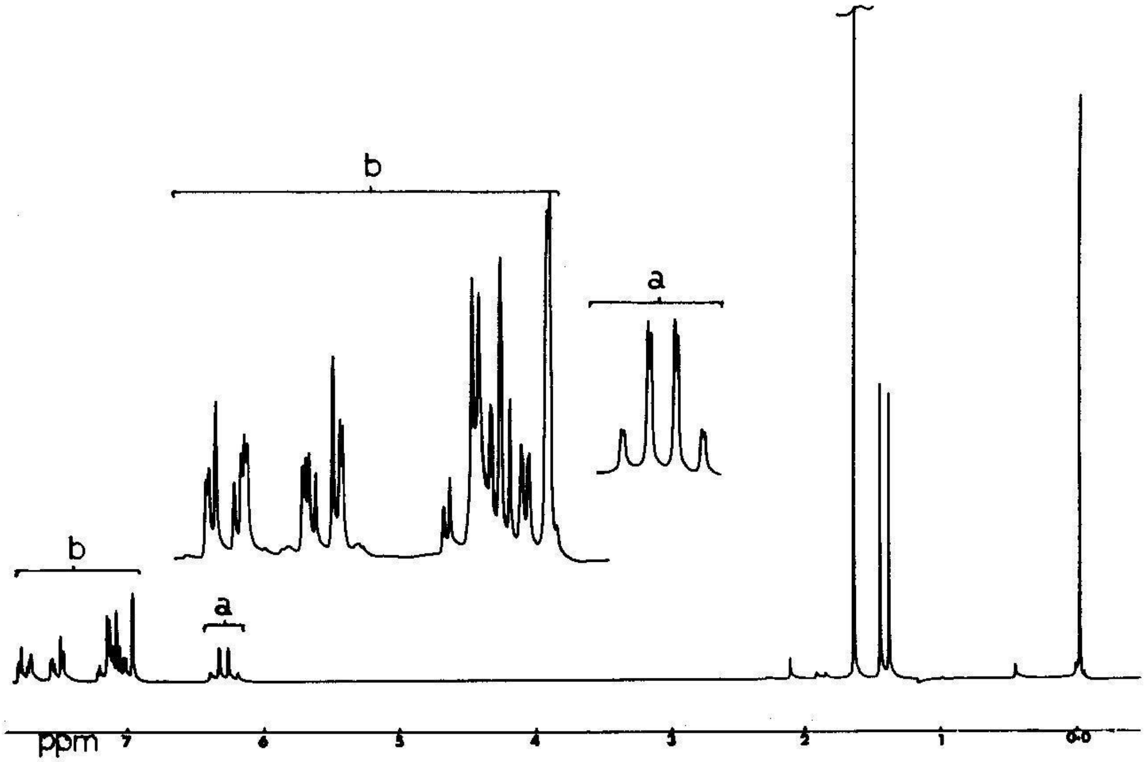


Fig. 1: ^{1}H NMR spectrum at 100 MHz of 1-(3-benzo[b]thienyl)-ethyl acetate dissolved as a 10% by weight solution in benzene-d_6, an example of an ABCD Spectrum.

further splitting due to long range coupling with H_3. On the remaining compounds (X=4,5,6 and 7), the H_7 is also deshielded more than the H_4 as in benzo [b]-thiophene itself. This assignment is consistent with the spectra of the 5 and 6-substituents, hence, H_4 or H_7 appears as strong doublet with small coupling to H_6 or H_5 respectively. It is well established that in a system containing two fused six-membered rings, a methyl substituent deshields the peri-proton.[17-19] However, in 3-methyl and 4-methyl benzo [b] thiophenes H_4 and H_3 are clearly shielded relative to benzo-[b] thiophene[8]. The case will be different in compound 3 (X-3). H_4 multiplet is deshielded and appears downfield than H_7, the deshielding effect is observed in different solvents. Large deshielding by 23 Hz was observed in benzene solution, Fig.1. The reversed peri-effect was observed in compound 4 with deshielding of H_3 signal, in the different solvents (e.g. in benzene, the deshielding was 39 Hz, Table 2). Also, the reversed peri-effects deshielding were observed of H_{10} in different solvents (Tables 1 & 2).

Van der Waals interactions are probably responsible for the peri-deshielding in naphthalene derivatives.[17-18] However, the conformation of the ethylacetate group and the size of the bond angles may be responsible for deshielding distance of H_4 and H_3 (X=3 and X=4). Substituent on the benzene ring (X=4) shows a much larger deshielding of H_3 signal in different solvents (see Tables 1 and 2). However, in compound 4,H_2 and H_3 are readily assigned, they consist of AB system with small coupling constants compared with benzenoid protons coupling constants.

A strong evidence gained from the analysis of the spectra of compounds 3 and 4 after the addition of induced shift reagent, Eu(FOD)$_3$[20]. The benzenoid protons treated as ABCD systems, (in both X = 2 and 3). When X=3, H_4 multiplets shows a significant downfield shift compared with H_2 shift. Considering bond numbers H_2 was closer to the coordinated site than H_4, the same results observed for compound 4, (X=4), H_3 signal demonstrates downfield shift more than H_5. H_5 was closer to the coordinated site than H_3

Fig. 2 and 3. This observation supports the above peri-deshielding of H_4 and H_3 of compounds 3 and 4 respectively. This is contrary to the ^{13}C NMR analyses of the same compounds.[21] A substantial upfield shift was observed at C-3 arising from peri-interaction of the H_3 and ethylacetate substituent, X=4. The same upfield shift was observed for H_3 and H_4 signals as a result of peri-interaction of the 3 and 4 methyl groups in 3 and 4-methyl benzo [b] thiophenes respectively.[8] Indeed, we found that, it is not necessary to observe upfield shift arising from ^1H signal and expecting upfield shift of ^{13}C signal of the same carbon attached to the same proton.

This was proved by recording the ^1H NMR Signals of H_{11} and H_{12}, the ^1H NMR spectra show that methyl protons signal of C-12 predominantly appears downfield than the methyl protons of C-11 (Tables 1,2). ^{13}C chemical shifts of C-11, C-12 are only 1 ppm apart,[21] the C-12 signal appears sometimes downfield or upfield of C-11 depending on the position of ethylacetate substituent. We found that the carbon chemical shift of C-11 signal in compounds 2,4,6 and 8 appears downfield than C-12 signal (opposite to ^1H NMR appearance).

Recent studies on 1,4-naphthoquinones[22] with shifts reagents show a significant downfield shifts of both the peri H_8 and the adjacent quinonoid H_2 (i.e. 3-methylamino-5-methoxy-1,4- naphthoquinone). Effect of 2-and 3-subtituents on H_5, H_6 and H_7 : The presence of an ethylacetate group in the 2-position produces a general shielding of the benzene ring protons. The shielding is strongest at the 4 and 7 positions. Substitution in the 3- position produces a general deshielding except that H_7 in the acetone and chloroform experience upfield shift, (see Tables 1 and 2). 1- (X-benzo [b] thienyl) ethyl acetate, X = 4, 5, 6 and 7:

The assignments of resonances were based on the known[14] relative magnitudes of the coupling constants between ortho, meta, and para protons in benzenoid rings, and on the expectation of $J_{2\,3}$ being appreciably smaller than J_{ortho} but large than J_{meta}[14] and further evidence come from the analysis of the spectra after adding lanthanide shift reagents. When X= 4 to 6, one of the ABCD patterns is missing and ABX pattern produced often spreads over a much wider range and simple spectra were obtained. In each case the ABX system can be analysed readily. H_2 and H_3 are clearly analysed as AB system with cross-ring couplings. The results are given in Tables 1 and 2.

The case will be different when X=7; in acetone H_4, H_5 and H_6 spectra are similar to the computed AA'X (deceptively simple) spectra[15,23], H_4 (X) signal appears as a triplet and H_5 and H_6 are equivalents (AA'), and appear as a doublet (Fig. 4.). H_2 and H_3 signals appears as AB system. However, in the other solvents ABX pattern produced (see tables).

Addition of shift reagents to compounds 4 to 7: The resultant spectra treated as AMX system (or ABC first order spectra)[20,24] for the benzenoid protons and AB system for H_2 and H_3 Fig. 5.

The effects of substitution of ethylacetate group at 4-position, a general downfield shift is produced in the different solvents, except that H_7 shows upfield shift. Substitution at 5-position produce upfield shift to both benzenoid and fused thiophene protons, (Table 1). Substitution at 6-position in chloroform, shows a little shielding. In acetone, little downfield shift recorded, but in benzene, only H_5 and H_7 experience downfield shift. Substitution of ethylacetate group at 7-position, showed in different solvents a general downfield shift except that H_4 shows upfield shift, these results are comparable with the results obtained from compound 4, in which H_7 shows upfield shift, this indicate that ethylacetate group substituted at benzenoid fused ring may lead to general para upfield shift (see Tables 1 and 2). The AB pattern arising from H_2 and H_3 in compound 1,4,5,6 and 7 are in good agreement with the calculated two spin system i.e. AB spectra. th different $\Delta\gamma/J$ ratios[15]

Use of Lanthanide shift reagents (LSR):
chemical shifts of the ring side chain protons (H_{10}, H_{11} & H_{12}) illustrate that H_{10} strongly affected by LSR than H_{12} while H_{11} is less affected by LSR than H_{12}. The same results obtained by addition of Eu $(FOD)_3$ to 1-phenylethyl acetate and 1-phenylethyl alcohol. This may indicate that the oxygen atom of the ester group is the favoured binding site than the carbonyl oxygen.

Coupling constants:

The observed coupling constants for the compounds under investigation are collected in Table 3. It can be seen from Table 3 that meta-coupling $J_{4,6}$ and $J_{5,7}$

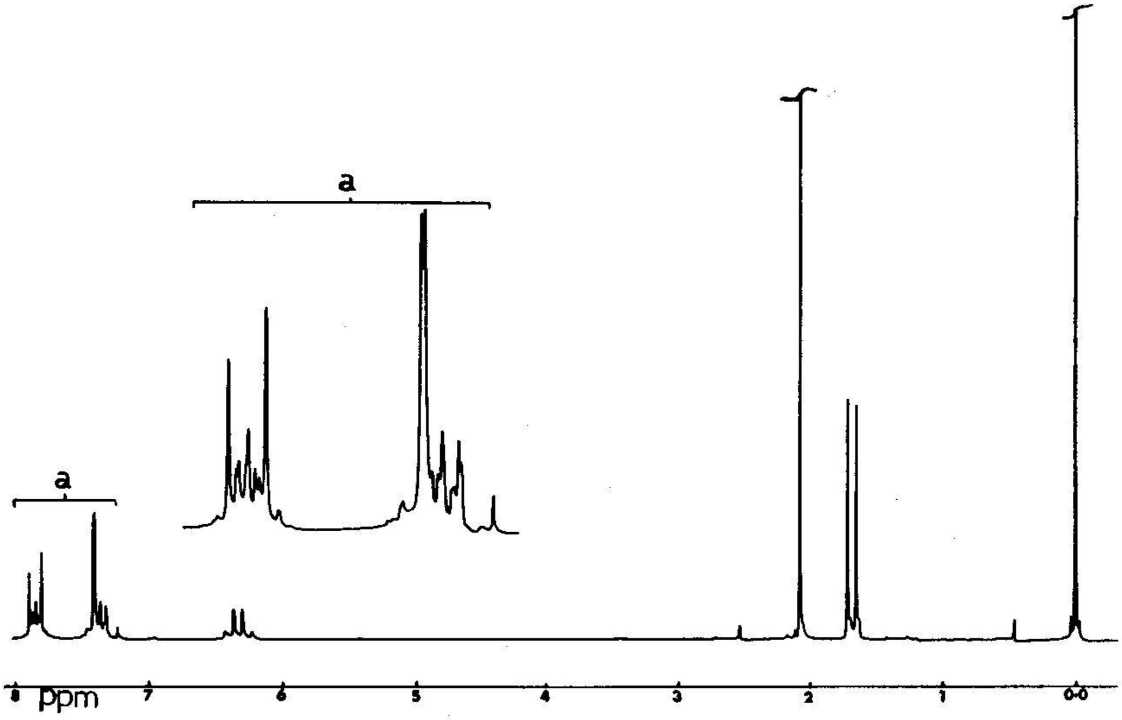


Fig. 2: ^{1}H NMR spectrum at 100 MHz of 1-(3-benzo[b]-thienyl)ethyl acetate 0.1 mol in chloroform-d

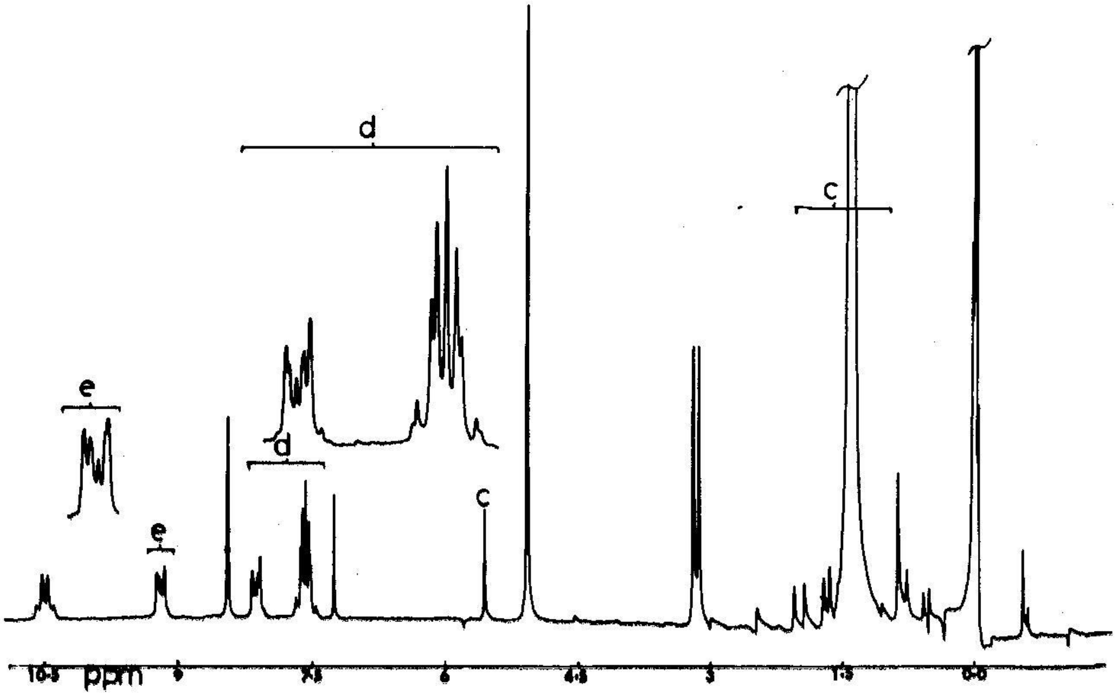


Fig. 2: b) Spectrum of (a) after the addition of 0,2 mol of $Eu(FOD)_3$. Upper superimposed traces run at higher gain. Peak sign c due to reagent.

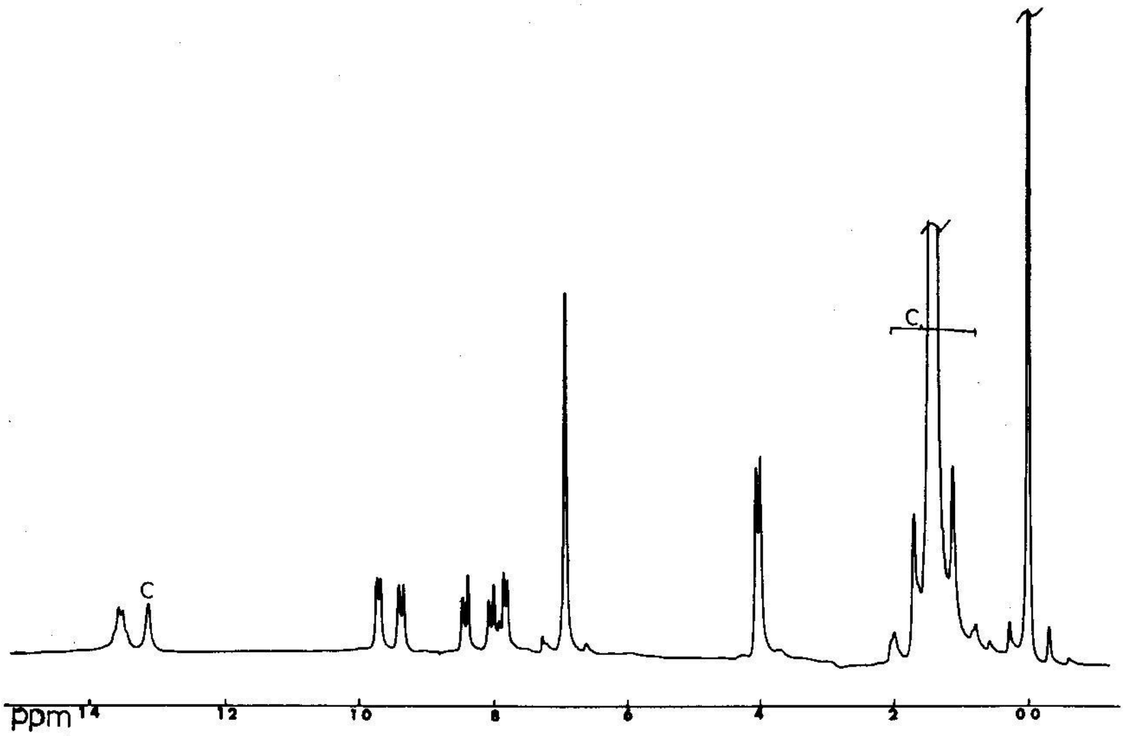


Fig. 3: ^{1}H NMR spectrum of 1-(4-benzo[b] thienyl)ethyl acetate 0.1 mol in chloroform-d after the addition of 0.3 mol of Eu(FOD)$_3$, peak sign c due to reagent.

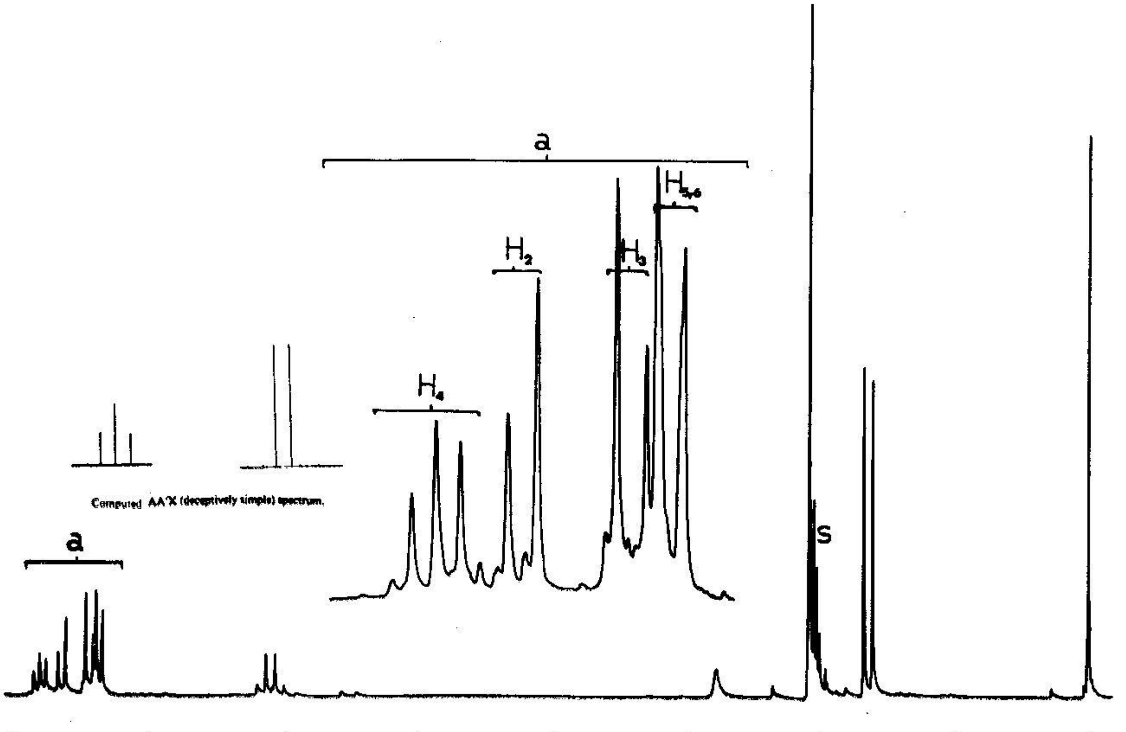


Fig. 4: ^{1}H NMR spectrum of 1-(7-benzo[b] thienyl)ethyl acetate 0.1 M in acetone-d_6. Top left trace is the computed AA'X spectra reference[23]. The observed splitting of 4.52 Hz is about what would be expected as the average of J_{AX} and $J_{A'X}$ S = Acetone-d_6

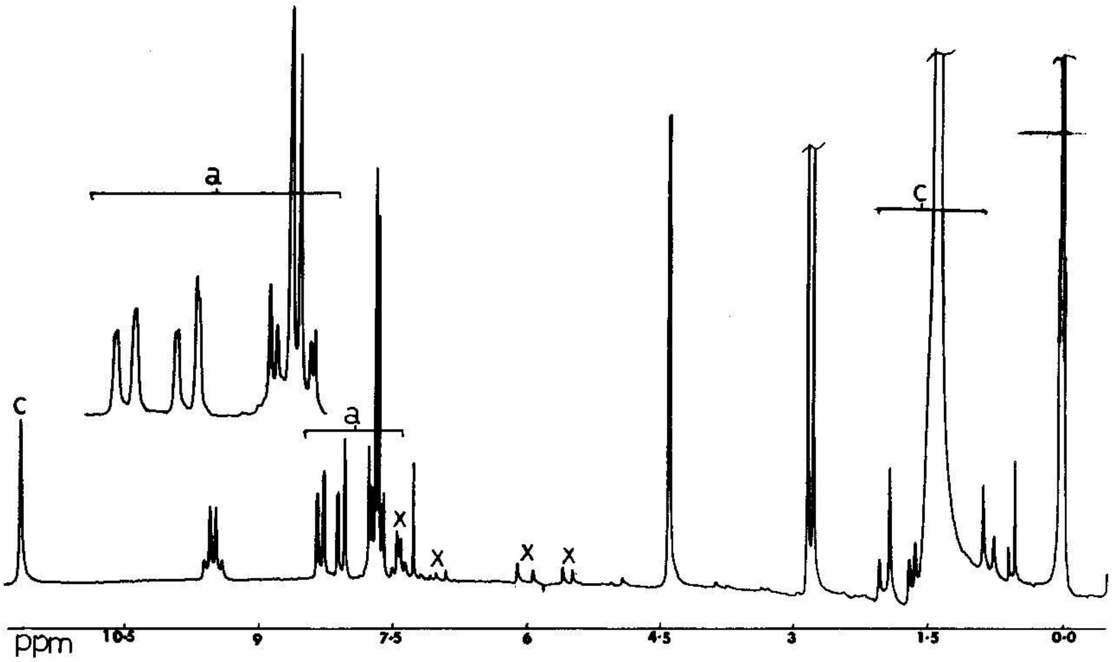


Fig. 5: ^{1}H NMR Spectrum of 1-(7-benzo[b]thienyl)ethyl acetate 0.1 mol in Chloroform-d after the addition of 0.3 mol of Eu(FOD)$_3$ Peak Sign C due to reagent, X traces of decomposed Starting Compound. Upper Superimposed traces (a), run at higher gain.

Table 3. Coupling Constants (Hz) in Benzo[b] thiophene and Substituted Benzo[b] thiophenes

Substituent	$J_{2,3}$	$J_{3,7}$	$J_{4,5}$	$J_{4,6}$	$J_{4,7}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$	$J_{4,5}+J_{6,7}$	$J_{5,7}+J_{6,7}$	$J_{10,11}$	
None a	5.45	0.84	8.04	1.21	0.74	7.14	1.06	8.13	9.25	9.19	–	
2–R b	—	0.73	—	—	0.73	—	—	8.05	—	—	6.59	$J_{3,10}$=0.73
c	—	0.73	8.04	1.20	0.73	7.14	1.06	8.06	9.16	9.16	6.59	
3–R	—	—	—	—	0.73	—	—	—	—	—	6.59	$J_{2,10}$=0.73,
	—	—	8.00	1.20	0.73	7.14	1.10	8.06	9.16	9.16	6.59	$J_{2,6}$=0.61 in benzene.
4–R	5.49	0.73	—	—	—	7.14	1.09	8.05	—	—	6.59	
	5.49	—	—	—	—	7.14	—	8.05	—	9.22	6.59	
5–R	5.49	0.73	—	1.80	0.73	—	—	8.34	—	—	6.59	
	5.49	—	—	1.80	—	—	—	8.34	—	—	6.59	
6–R	5.49	0.73	8.05	—	0.73	—	1.28	—	—	—	6.59	
	5.49	—	8.05	—	—	—	1.28	—	—	—	6.59	
7–R	5.49	—	8.05	1.22	—	7.14	—	—	—	—	6.59	
	5.49	—	8.05	1.22	—	7.14	—	—	9.27	—	6.59	

In case of 1-phenyletheyl acetate and 1-phenylethyl alcohol, J_{ortho}=7.3±0.18 Hz (after the addition of 0.3M Eu (FOD)$_3$ to 0.1M substrate in chloroform-d solution).

(1) Coupling constants obtained from the Eu (FOD)$_3$-shifted spectra are good to at least ± 0.18 Hz while those obtained from the 100 MHz spectra are good to at least ± 0.12 Hz.

a = measured in chloroform-d and in agreement with data in ref.40.

b = measured in different solvents.

c = measured after the addition of Eu (FOD)$_3$, (0.3M) to chloroform-d solution of substrate (0.1M).

across the substituent is larger than the values obtained for benzo [b] thiophene itself. The same results observed for substituted benzene[25] and quinolines[26]. The magnitude of $J_{2,3}$ appears to be not affected by substitution of ethyl acetate group in the benzenoid ring and is similar to that observed for other benzo [b] thiophenes[27,28]. Coupling constants obtained from shifted spectra have not received careful attention regarding their validity. However, reports have been suggested that coupling constants from shifted spectra of both σ[29] and π[30] systems are unaffected by the shift reagent. Others report a case in which a shift reagent does effect the values of coupling constants.[31] In this work, coupling constants obtained before (when its feasible) and after the addition of LSR's show no appreciable change in the coupling constants, the small changes are with in the experimental errors.

Cross-ring coupling

Long-range coupling between protons in different rings is now a well established feature of the NMR spectra of polycyclic systems[32,33]. In most spectra the signals due to H_3 and H_7 are clearly resolved, ($J_{3,7} = J_{4,7}$, see Table 3).

Ring-side chain coupling

The coupling between H_{10} of the ethylacetate group and the ring proton H_3 or H_2 (compound 2 and 3 respectively) is of great interest. Thus the coupling between the protons H_{10} and H_3 (or H_2) which are four bonds apart, is 0.73 Hz. Large values were recorded for different heterocyclic compounds of different substituent.[32] The main difference (ca. 0.37 Hz) could be due to the size of the ethylacetate group. The bulkiness of ethylacetate group compared with methyl group could in fact prevent any "through-space" coupling mechanism associated with the proximity of the hydrogen atoms in the two C-H bonds. This effect has recently explained theoretically by Barfield and others[34-36] Similar results have been reported for coupling between N-Methyl and adjacent ring C-H protons of purines and pteridines ($^4J_{N\text{-}CH_3,\ C\text{-}H} = 0.5$ Hz)[37]. It is interesting to point out that when ethylacetate group is substituted in positions 4 to 7, a broad quartet for H_{10} has been noticed in different solvents. The broadness in the quartet could be due to a very small additional splitting by the protons of the benzenoid ring, compared with H_2 and H_3.

Experimental:

All NMR spectra were measured on JEOL JNM FX-100 spectrometer operating at 100 MHz in the Fourier Transform Mode. All the spectra were recorded at ambient temperature 25° and over 1000 and 1500 Hz sweep width using 16 K data points. Chemical shifts are in δ units (part per million) from internal TMS. Heterocyclic compounds of the title were prepared by known methods[38,39]. The LSR used in these studies was Europium (III) -tris- (1,1,1,2,2,3,3,- heptafluoro-7, 7,-dimethyl-4,6-octadionate), Eu $(FOD)_3$, was supplied by FLUKA AG. The solutions of shift reagent were prepared freshly prior use, but generally no further precautions were taken to exclude moisture.

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