Conformational Analysis of Organic Carbonyl Compounds. Part 3.[1,2] A ^1H and ^{13}C Nuclear Magnetic Resonance Study of Formyl and Acetyl Derivatives of Benzo[*b*]thiophen

Rois Benassi, Ugo Folli, Dario Iarossi, Luisa Schenetti, and Ferdinando Taddei *
Istituto di Chimica Organica, Università, Via Campi 183, 41100 Modena, Italy

The conformational analysis of formyl and acetyl derivatives of benzo[*b*]thiophen was carried out by employing n.m.r. chemical shifts (^1H and ^{13}C) and coupling constants. By measuring the lanthanide-induced shifts (LIS) and simulating experimental chemical shifts the relative conformer stability was determined. The results show that all the molecules examined are present almost completely in the *Z*-conformation and that the stabilization of one conformer in this heterocyclic system seems due almost exclusively to the mesomeric interaction originating in the *trans*-arrangement of the C=O bond and the C=C bond having the higher double-bond character.

In organic compounds containing a carbonyl group bonded to an unsaturated, aromatic, or heteroaromatic system conformationally non-equivalent structures arise as a result of restricted rotation around the C–C(O) bond. Several theoretical and experimental studies [1-10] have been reported in the last 20 years concerning the energy barrier and relative conformer stability. Among experimental methods ^1H and ^{13}C n.m.r. have been proved to be the most powerful tool. Variable-temperature studies may provide the energy barriers and relative isomer populations, while this latter information may also often be acquired by employing long-range coupling constants and chemical shifts.

Lanthanide-induced shifts (LIS) have been widely employed as a reliable method [11-17] for determining the relative isomer population in the case of fast rotation (relative to the n.m.r. time scale).

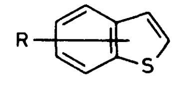
Previously [1,2] we have examined the conformational properties of the formyl and acetyl groups both by testing the practical applicability of MO semi-empirical and *ab initio* methods in the prediction of energy barriers and relative isomer stability and by performing conformational analysis of a number of derivatives of condensed hydrocarbons.

In the formyl and acetyl derivatives of benzo[*b*]thiophen, as regards position 4, one expects, in principle, to find a situation similar to that of position α in naphthalene, while the 2-substituted derivative should show a situation close to that of the same substituted derivative of thiophen. The latter hypothesis has been confirmed experimentally,[18-20] since the aldehyde is present almost completely in the *Z*-conformation. As regards substitution at position 7, the situation may differ from that of the α-position in naphthalene owing to the presence of the sulphur atom in the neighbouring ring and even for the 3-substituted compound differences may arise in respect of 3-substituted thiophen owing to the presence of the condensed ring.

With the aim of analysing the conformational properties of the acetyl and formyl groups in the benzo[*b*]thiophen system, we studied derivatives (1)—(4). The conformational analysis of these molecules has been carried out by examining their ^1H and ^{13}C chemical shifts, long-range proton–proton coupling constants, and by employing the LIS method for a quantitative estimate of conformer populations.

Experimental

The n.m.r. spectra of compounds (1)—(4) were recorded in [^{2}H]chloroform solution (0.3M) at 200 MHz for ^1H and 50.3088 MHz for ^{13}C by employing a Varian XL 200 spectrometer. The shift reagent employed is Eu(fod)$_3$, purified by sublimation *in vacuo* and kept in a dry atmosphere, added in known amounts to solutions of the substrate examined. The experimental results were elaborated according to the procedures reported by Montaudo and his co-workers.[15] All calculations were performed on a Cyber 76 CDC computer.



(1a) R = 2–CHO (1b) R = 2–MeCO
(2a) R = 3–CHO (2b) R = 3–MeCO
(3a) R = 4–CHO (3b) R = 4–MeCO
(4a) R = 7–CHO (4b) R = 7–MeCO

Benzo[*b*]thiophen-2-,[21] -3-,[22] -4-,[23] and -7-carbaldehyde,[23] and 2- [24] and 3-acetylbenzo[*b*]thiophen [25] were prepared by known methods.

4- and 7-acetylbenzo[*b*]thiophens were prepared in yields higher than 70% from the corresponding carboxylic acids [23] by employing the general method for the synthesis of ketones through the diethyl acylmalonate [26] derivatives. The compounds gave correct elemental analyses and the following physical properties: 4-acetylbenzo[*b*]thiophen, b.p. 100—102 °C at 0.25 mmHg, n_D^{14} 1.6500; 7-acetylbenzo[*b*]thiophen, b.p. 115—117 °C at 0.7 mmHg, n_D^{20} 1.6428 (lit.,[27] 124—126 °C at 1 mmHg, $n_D^{19.7}$ 1.6397).

Results and Discussion

The ^1H chemical shifts (δ values) and ^1H–^1H coupling constants are reported in Table 1. ^{13}C Chemical shifts (δ values) and $^1J_{CH}$ values are collected in Table 2. The ^1H spectra were fully analysed by employing the LAOCOON 3 program.[28] The assignment of ^{13}C chemical shifts was performed on the basis of various experimental procedures: by examining the pattern of proton-coupled spectra, employing the off-resonance technique varying the decoupling frequency in order to correlate the corresponding δ_C and δ_H values, by selective decoupling and by following the chemical shift changes determined by the shift reagent.

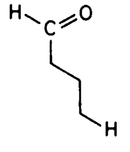
The ^1H resonance spectra show the presence of two long-range inter-ring coupling constants, *i.e.* J_{26} and J_{37}. The latter coupling constant, which is higher in all the compounds examined, should occur over five bonds according to previous studies,[29] while J_{26} should involve a six-bond coupling across the sulphur atom,[30] both along a zig-zag path. No other inter-

Table 1. ^1H Chemical shifts (δ values) and proton–proton coupling constants (Hz) in formyl and acetyl derivatives of benzo[*b*]thiophen

Compound	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_{CHO} or δ_{CH_3CO}
(1a)		8.02	7.93	7.43	7.49	7.89	10.09
(2a)	8.30		8.67	7.50	7.45	7.87	10.13
(3a)	7.73	8.39		7.86	7.53	8.15	10.25
(4a)	7.65	7.43	8.10	7.57	7.87		10.23
(1b)		7.93	7.88	7.40	7.45	7.86	2.64
(2b)	8.25		8.76	7.48	7.41	7.85	2.63
(3b)	7.64	8.37		7.94	7.41	8.07	2.72
(4b)	7.62	7.39	8.04	7.47	8.00		2.75
Benzo[*b*]thiophen [a]	7.36	7.27	7.74	7.28	7.26	7.81	

	J_{23}	J_{26}	J_{37}	J_{45}	J_{46}	J_{47}	J_{56}	J_{57}	J_{67}
(1a)			0.89	8.30	1.15	0.79	7.20	1.13	8.23
(2a)		0.41		8.21	1.23	0.77	7.17	1.04	8.20
(3a)	5.56		0.73				7.38	0.95	7.99
(4a)	5.48	0.37		7.91	1.11		7.28		
(1b)			0.69	8.12	1.10	0.80	7.07	1.00	8.33
(2b)		0.36		8.29	1.23	0.65	7.12	1.03	8.24
(3b)	5.60	0.43	0.86				7.52	0.94	8.03
(4b)	5.57	0.45		7.87	1.01		7.55		
Benzo[*b*]thiophen [a]	5.57	0.30	0.86	8.09	1.16	0.73	7.22	1.17	8.06

[a] Ref. 30*a*.



(A)

ring long-range coupling is observed under our experimental conditions (resolution *ca.* 0.2 Hz). The remaining observed proton–proton coupling constants referred to the ring protons are in the range of those reported for the unsubstituted benzo[*b*]thiophen molecule.[30] No long-range coupling constant was observed involving the aldehyde proton and protons of the ring. Since the coupling constant over five bonds involving the aldehyde proton amounts to 0.4—0.5 Hz for the *E* conformer in the formyl derivatives of naphthalene [2] and is typical of one arrangement of the type (A) while it should be very near to zero for the opposite arrangement of the formyl group, the absence of a measurable value (>0.1 Hz) for this coupling should indicate, at least for compounds (3a) and (4a), that the *Z*-form is the more populated one.

Qualitative indications of the conformation of the carbonyl group may be also obtained by examining proton chemical shifts in comparison with those of the unsubstituted molecule. With respect to the low-field shift caused by carbonyl substituents in the 2- and 3-positions on the adjacent proton of the five-membered ring, these prove to be of the same order of magnitude as those observed in the corresponding substituted thiophens; [20] only for the 3-CHO derivative does the low-field shift of 2-H turn out to be larger in the benzo[*b*]thiophen molecule than in the corresponding thiophen derivative, amounting to 0.94 and 0.79 p.p.m., respectively. This probably reflects a larger amount of the *Z*-form in the former compound. On a qualitative basis these results confirm that the conformation of the formyl and acetyl groups in compounds (1a), (2a), (1b), and (2b) should correspond to a predominant *Z*-form as occurs in the corresponding thiophens.[18-20,31,32] In the 3-substituted derivatives even the chemical shift of 4-H is significant and confirms the above conclusion: in both compounds (2a and b) this proton moves >1 p.p.m. to low-field with respect to the unsubstituted derivative resembling what happens to 8-H of naphthalene-1-carbaldehyde [2] and 1-acetylnaphthalene.[2,33] When the carbonyl substituent is in position 4, compounds (3a and b), the low-field shift with respect to the unsubstituted compound is of the order of 1.1 for 3-H and 0.6 p.p.m. for 5-H. These results, when compared to those of 1-naphthalene derivatives, indicate that the *Z*-conformer should be the most populated, even for compounds (3a and b). Analogous conclusions may be reached for the 7-substituted carbonyl derivatives (4a and b) on comparing the low-field shift of 6-H (0.6 p.p.m.) with that of 2-H in 1-naphthalene derivatives, and concluding, thus, that in these derivatives the carbonyl oxygen faces the sulphur atom of the heterocyclic ring.

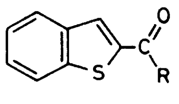
These conclusions are corroborated by the behaviour of ^{13}C chemical shifts if one refers to the shift induced by carbonyl substituents in respect of unsubstituted derivatives ($\Delta\delta_C$). For the 3- and 4-CHO derivatives C-3a, and for the 7-CHO derivative C-7a, are shifted 2—4 p.p.m. upfield, *i.e.* the same order of magnitude as the effect induced on the carbon atoms of the corresponding positions in naphthalene-1-carbaldehyde.[7] For benzo[*b*]thiophen-2-carbaldehyde the differences in chemical shift induced by the formyl substituent with respect to the unsubstituted derivative ($\Delta\delta_{C\text{-}2}$ and $\Delta\delta_{C\text{-}3}$) are very close to those produced by this substituent on thiophen,[34] and this may be assumed to be a further indication that the same conformational situation of the formyl group is present in both systems. Analogous conclusions are derived for the corresponding acetyl derivatives.

In Table 2 the one-bond coupling constants $^1J_{CH}$ for the derivatives (1)—(4) are also collected. While, in general, these coupling constants are close to those for thiophen and naphthalene in terms of the five- and six-membered rings of substituted benzo[*b*]thiophen, the values for the coupling constants relative to those protons which should face the carbonyl oxygen are observed to increase by a few Hz. This is the case of $^1J_{C\text{-}H\text{-}4}$ in compounds (2a and b) and $^1J_{C\text{-}H\text{-}3}$ in compounds (3a and b). This effect seems to be also present in formylnaphthalenes, as may be observed from the values reported in the literature [6] for $^1J_{C\text{-}H\text{-}8}$ in naphthalene-1-carbaldehyde and $^1J_{C\text{-}H\text{-}3}$ in naphthalene-2-carbaldehyde. Thus

Table 2. ^{13}C Chemical shifts (δ values) and $^{1}J_{CH}$ coupling constants (Hz) (in parentheses) in formyl and acetyl derivatives of benzo[*b*]thiophen

Compound	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_{3a}	δ_{7a}	$\delta_{C=O}$	δ_{CH_3}
(1a)	143.38	134.39	126.25	125.25	128.15	123.30	138.55	142.69	184.61	
		(168.82)	(162.10)	(161.31)	(160.34)	(163.80)			(179.53)	
(2a)	143.22	136.51	124.78	126.09	126.15	122.41	135.17	140.45	185.34	
	(183.41)		(166.76)	(160.39)	(161.75)	(163.12)			(175.02)	
(3a)	130.58	123.06	130.67	131.19	123.64	128.39	137.20	141.69	192.21	
	(185.60)	(175.35)		(161.30)	(164.42)	(163.55)			(174.35)	
(4a)	130.28	122.70	129.61	124.06	131.20	130.64	141.10	136.82	191.21	
	(183.93)	(170.50)	(161.11)	(163.43)	(161.10)				(176.55)	
(1b)	143.95	129.62	125.88	124.98	127.40	122.98	139.11	142.60	192.18	26.77
		(168.05)	(161.61)	(160.99)	(160.72)	(164.40)				(128.30)
(2b)	137.31	135.51	125.76	125.81	125.42	122.19	136.46	139.83	193.00	28.18
	(182.46)		(163.36)	(160.22)	(160.68)	(162.39)				(127.49)
(3b)	129.31	124.90	132.07	127.23	123.27	127.38	137.46	141.79	197.52	27.93
	(184.65)	(175.27)		(158.65)	(162.31)	(163.12)				(127.63)
(4b)	130.87	122.67	128.78	123.78	127.06	130.81	141.13	137.94	197.33	26.21
	(182.23)	(169.49)	(161.04)	(161.70)	(159.16)					(127.79)
Benzo[*b*]thiophen [a]	126.1	123.65	123.50	124.0	124.05	122.30	139.45	139.60		

[a] Ref. 34*b*.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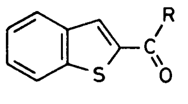
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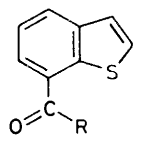
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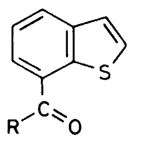
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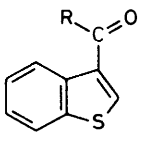
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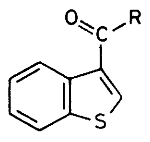
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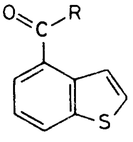
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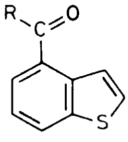
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it appears that accurate values of one-bond carbon–proton coupling constants may be employed as a conformational probe for carbonyl substituents.

To place the conformational properties of the formyl and acetyl groups in compounds (1)—(4) on a more quantitative basis, the compounds were analysed by the LIS method. Analysis of the experimental results was performed by employing the McConnell and Robertson [35] equation and assuming that the interaction between lanthanide and substrate is entirely or predominantly of a dipolar nature. Further, the equimolar lanthanide–substrate complexes were considered to have axial symmetry and a constant geometry was maintained in the different conformers. The population ratio was determined by employing expression (1), where G_{1i} and G_{2i},

$$\Delta\delta_i = K(\chi_1 G_{1i} + \chi_2 G_{2i}) \qquad (1)$$

according to Montaudo and his co-workers,[16] are the geometrical factors corresponding to the *i*th nucleus in the two conformers, χ_i their molar fractions, K the pseudocontact constant, and $\Delta\delta_i$ the LIS corresponding to the *i*th nucleus. The oxygen atom of the carbonyl group was chosen as the complexation site and the mean position of the lanthanide atom is defined by the three polar co-ordinates [16] R, φ, and ω: by labelling Ld the lanthanide atom, R represents the Ld–O distance and is commonly assumed [36] to be 3 Å for the Eu atom, φ is the Ld–O–C internuclear angle, and ω the dihedral angle Ld–O–C–C(H$_3$) (for acetyl derivatives) according to the lanthanide–substrate configuration assumed in ref. 16. For each proton in a given conformation the geometrical factors G in equation (1) may be thus calculated for a given set of R, φ, and ω values and they allow a determination of the conformer populations χ by least-squares minimization between observed and calculated LIS values. The most likely molar fractions χ are identified with those corresponding to the minimum value of the Hamilton agreement factor (A.F.).[15]

For the simulation of the LIS proton spectra, the simpler one-site model (OSM) was preferred to the alternative two-site model (TSM) which accounts for complexation to the two oxygen lone-pairs. It has in fact been recently reported [37] that both models give comparable satisfactory results when applied to the simulation of LIS spectra. To obtain the populations of the conformers of the formyl and acetyl groups, four different $\Delta\delta_i$ values are therefore required. The molecular geometry of the compounds was constructed from that of 5-bromo-2,3-dimethylbenzo[*b*]thiophen [38] as regards the heterocyclic ring, while for the formyl and acetyl groups the following bond distances were employed: C=O, 1.22; C–H, 1.085; C–C(exocyclic), 1.485; C–C(H$_3$), 1.513 Å; the bond angles were chosen to be perfectly trigonal. The aldehyde proton and

Table 3. Experimental and calculated (in parentheses) LIS values, molecular geometry parameters of the complexes, and relative amounts of conformational isomers in formyl and acetyl derivatives of benzo[*b*]thiophen

Compd.	2-H	3-H	4-H	5-H	6-H	7-H	CHO/CH$_3$	*K*	φ (°)	ω (°)	A.F.	% *Z* con-former
(1a)		3.40 (3.40)	1.28 (1.29)	0.87 (0.86)	0.98 (0.96)	1.62 (1.62)	11.23	633.44	30	10	0.0061	94
(2a)	4.88 (4.92)		14.33 (14.35)	2.38 (2.48)	1.93 (1.73)	2.30 (2.13)	15.08	899.38	45	0	0.018	100
(3a)	1.44 (1.45)	8.93 (8.93)		3.26 (3.26)	1.60 (1.60)	1.46 (1.46)	9.40	536.62	45	0	0.003 05	96
(4a)	2.14 (2.15)	1.94 (1.91)	1.87 (1.90)	1.88 (1.88)	3.62 (3.62)		10.72	834.11	25	40	0.0081	100
(1b)		4.57 (4.57)	1.13 (1.18)	0.71 (0.66)	0.62 (0.66)	1.27 (1.25)	6.95	827.45	25	0	0.017 77	84
(2b)	5.68 (5.71)		13.03 (13.04)	0.85 (0.78)	1.01 (1.00)	1.79 (1.67)	11.16	851.71	60	30	0.0099	84
(3b)	0.82 (0.89)	13.01 (13.01)		5.36 (5.41)	2.54 (2.37)	2.08 (1.94)	10.79	767.57	60	20	0.0165	86
(4b)	0.70 (0.73)	1.21 (1.12)	1.45 (1.44)	1.66 (1.73)	3.63 (3.62)		6.15	572.55	55	30	0.0267	93

the methyl group were excluded from LIS simulation since their $\Delta\delta_{\mathrm{lim}}$ are affected by contact contributions.

The experimental $\Delta\delta_{\mathrm{lim}}$ referring to the protons of compounds (1)—(4), the molecular geometry parameters of the complexes and relative amounts of conformers are reported in Table 3. The results show that for all derivatives the *Z*-conformer is the prevailing one, thus confirming the conclusions reached on a qualitative basis from ^{1}H and ^{13}C chemical shifts. Measurements at low temperature (–150 °C) failed to show separate signals for the conformers and consequently also to measure directly their relative amounts.

The *Z*-configuration in compounds (1)—(4) is characterized by a *trans*-arrangement of the C=O bond and the shorter adjacent C=C bond of the ring having higher double bond character. Thus for the 3- and 4-CHO derivatives the situation may be likened to that of naphthalene-1-carbaldehyde,[2,7] while for the 2-CHO derivative the situation of thiophen-2-carbaldehyde [18-20] is present. Even in this case the *trans*-arrangement of the C=O and C=C bonds seems to be the rule [18-20] when no bulky substituent is present in position 3. For the 7-carbonyl derivatives this arrangement is again present in the more stable conformer. To explain the stability of the *Z*-conformation in naphthalene-1-carbaldehyde a hydrogen bond-type interaction between the carbonyl oxygen and the *peri*-hydrogen has been invoked.[39] This interaction cannot take place in compounds (4a and b) and the mesomeric interaction generated by the *trans*-arrangement of the C=O and the shorter C=C bond should mostly account for the extra stability of the *Z*-conformer. An attractive electrostatic interaction between the negative carbonyl oxygen and a supposed [40] positive sulphur atom of the heterocyclic ring must probably be ruled out [19] and is, in any case, unnecessary to explain the stability of the *Z*-conformer in thiophen-2-carbaldehyde.[19] From semi-empirical calculations in the CNDO/2 approximation [41] we find that the total charge density on the sulphur atom and on the carbonyl oxygen of compound (4a) is very small and, at least at this stage of approximation, theoretical calculations seem not to be conclusive in supporting the contribution of electrostatic positive interactions to the stability of the *Z*-conformer of this compound. Further, the CNDO/2 results predict correctly the relative stability of the planar conformers in the derivatives (1a)—(3a) but not in (4a), but the perpendicular conformation is more stable than the planar one, as verified also for other carbonyl derivatives.[1] This fact is unacceptable on several grounds and shows that CNDO/2, as already pointed out,[1] is not recommended for conformational studies of conjugated carbonyl compounds.

Acknowledgements

We are grateful to the Centro Strumenti and Centro di Calcolo, Modena University, for the use of the n.m.r. spectrometer and for computing facilities.

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Received 14*th June* 1982; *Paper* 2/994