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Carbon-13 NMR Spectra of 4-Chromanone, 4*H*-1-Benzothiopyran-4-one, 4*H*-1-Benzothiopyran-4-one 1,1-Dioxide, and Their Substituted Homologs

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The ^{13}C NMR spectra of 4-chromanone, 4*H*-1-benzothiopyran-4-one, 4*H*-1-benzothiopyran-4-one 1,1-dioxide, and their methyl and phenyl substituted homologs were examined. The salient effect depending on the kinds of the hetero atoms or the group at the 1-position has been observed on the chemical shifts, especially for C-2, C-3, C-8, C-4a, and C-8a.

^{13}C NMR spectroscopy has been used extensively to elucidate the structures of complex molecules. Although ^{13}C NMR studies of several flavones were performed in connection with the structural elucidation of naturally occuring flavonoid compounds,[1] its applications to this field have so far been limited.[2] We wish to report here a study of the ^{13}C NMR spectra of 4-chromanone (**2**), 4*H*-1-benzothiopyran-4-one (**7**), 4*H*-1-benzothiopyran-4-one 1,1-dioxide (**12**), and their methyl and phenyl substituted homologs, undertaken with the object of providing background data for use in future structural studies of the heterocyclic compounds.

Natural-abundance 25.15 MHz ^{13}C FT-NMR spectra in $CDCl_3$ were obtained using the ^{1}H noise-decoupling technique. The signals were assigned by comparing the signal shifts due to differences in structures between closely related compounds and by the use of the ^{1}H off-resonance decoupling technique. A shift reagent, $Yb(dpm)_3$ was used to aid the assignments of the resonances to specific carbon atoms.[3] The chemical shifts, δ, thus obtained are listed in Table 1, in which the carbon numbering relates, for purposes of comparison, to the equivalent carbon in the flavanone series (Fig. 1).

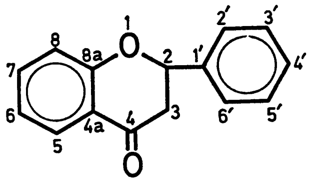


Fig. 1.

Results and Discussion

The resonance of the carbonyl carbon of 1-tetralone (**1**) occurs at δ 197.90. Upon the replacement of the 1-methylene group (the numbering system follows that of **2**) with a hetero atom, the carbonyl carbon signals moved upfield; that of **12** appears at the highest field among the simplest members of each series of compounds, **1**, **2**, **7**, and **12**. Analogous trends were observed in the ^{13}C NMR spectra of cyclohexanone and 1-hetera-4-cyclohexanones.[4] The substituent parameters of a sulfur and an oxygen atom, and a sulfonyl group in simple 1-hetera-4-cyclohexanones are negative (upfield shift) for a γ-carbon. The chemical shifts of C-2 and C-3 of **1**, **2**, **7**, and **12** also exhibited trends similar to those observed in the series of 1-hetera-4-cyclohexanones. The chemical shifts of C-2 are described in the order of the electron-withdrawing abilities of the atoms or the group at the 1-position. The C-3 resonances of **2** and **7** occur at a field lower, while that of **12** appear at one higher than that of **1**. The effect of the sulfonyl group in the C-3 chemical shift indicated a negative value, the reverse of those of the oxygen and the sulfur atom. This may be due to the steric γ-gauche interaction of C-3 with one of the oxygen atoms of the sulfonyl group, which takes an axial-like orientation.[4] The carbonyl chemical shifts of the 2-substituted compounds are similar to those of the corresponding parent compounds. On the other hand, the carbonyl signal of 3-methyl-4-chromanone (**4**) moved downfield by about 3 ppm.

On the addition of $Yb(dpm)_3$ to the solution examined, the carbonyl signal was moved downfield. The magnitude of the lanthanoid-induced shifts (LIS) of **12** and 1-thioflavanone 1,1-dioxide (**15**) were much smaller than those of **2**, flavanone (**5**), **7**, and 1-thioflavanone (**10**). Ytterbium ions may coordinate to the oxygen atoms of the sulfonyl group as well as to the carbonyl oxygen atom.

The signal of the methyl group at the 3-position resonates at an apparently high field (δ 10.55). This indicates that the through-bond interaction of the oxygen atom at the γ-position participates significantly, because the arrangement of the oxygen atom and the methyl carbon is anti-periplanar.[5] However, when a sulfur atom is introduced at the 1-position, the methyl signal appears at δ 13.8; the electronic γ-effect of a sulfur atom, the third-row hetero atom, is negligible.[5] The methyl resonance of 2-methyl-4*H*-1-benzothiopyran-4-one 1,1-dioxide (**13**) occurs at a field slightly higher than that of 2-methyl-4*H*-1-benzothiopyran-4-one (**8**) because of the steric γ-gauche interaction of the oxygen atoms of the sulfonyl group.

The resonances of substituted aromatic carbons are easily distinguished from those of other aromatic carbons by the off-resonance decoupling technique. Since the substituent parameters of the carbonyl group on both α- and β-carbons are positive, the former smaller than the latter, the signals at δ 144.39 and 132.56 of **1** can be ascribed to C-4a and C-8a respectively. The

TABLE 1. CARBON-13 NMR CHEMICAL SHIFTS OF 4-CHROMANONES, 4*H*-1-BENZOTHIOPYRAN-4-ONES AND 4*H*-1-BENZOTHIOPYRAN-4-ONE 1,1-DIOXIDE

No.	Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1	1-Tetralone	29.60	23.29	39.07	197.90	128.74	126.49	133.29	126.98
2	4-Chromanone Parent		66.92	37.61	191.47	126.96	121.19	135.75	117.76
	ΔYb[a]		2.79	5.83	13.05	4.08	1.79	1.48	1.76
3	2-Methyl-		74.20	44.47	191.96	126.86	121.09	135.78	117.82
4	3-Methyl-		72.25	40.77	194.20	127.32	121.25	135.44	117.70
5	2-Phenyl-(flavanone)		79.47	44.53	191.66	126.93	121.47	136.01	118.00
	ΔYb		2.43	5.52	12.86	3.99	1.75	1.34	1.58
6	3-Phenyl-(isoflavanone)		71.40	52.23	191.90	128.56	121.52	135.93	117.82
7	4*H*-1-Benzothiopyran-4-one Parent		26.45	39.37	193.54	128.98	124.80	133.05	127.40
	ΔYb		2.48	5.52	12.31	4.07	1.69	1.33	1.52
8	2-Methyl-		36.34	47.68	193.78	128.74	124.67	133.11	127.28
9	3-Methyl-		32.94	42.04	196.14	129.35	124.67	132.80	127.16
10	2-Phenyl-(1-thioflavanone)		45.32	46.53	194.02	129.04	125.04	133.47	127.10
	ΔYb		2.30	5.10	11.77	3.82	1.64	1.39	1.40
11	3-Phenyl-(1-thioisoflavanone)		32.51	53.63	193.66	129.59	124.80	132.99	127.22
12	4*H*-1-Benzothiopyran-4-one 1,1-dioxide Parent		49.44	36.82	190.08	128.74	(133.23)[b]	(134.81)	123.64
	ΔYb		1.50	1.83	4.00	1.27	(0.60)	(0.60)	0.73
13	2-Methyl-		54.66	44.28	190.26	128.44	(133.17)	(134.87)	124.19
14	3-Methyl-		55.51	41.37	193.23	128.68	(133.17)	(134.62)	123.34
15	2-Phenyl-(1-thioflavanone 1,1-dioxide)		63.76	42.95	190.81	129.76	(133.19)	(134.90)	124.19
	ΔYb		1.70	2.43	4.85	1.32	(0.66)	(0.54)	0.73
16	3-Phenyl-(1-thioisoflavanone 1,1-dioxide)		55.57	52.90	191.71	129.46	(133.64)	(134.98)	123.76

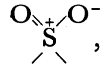
No.	Compound	C-4a	C-8a	Me	C-1′	C-2′,6′	C-3′,5′	C-4′
1	1-Tetralone	132.56	144.39					
2	4-Chromanone Parent	121.27	161.73					
	ΔYb	5.71	3.11					
3	2-Methyl-	120.79	161.62	20.93				
4	3-Methyl-	120.74	161.81	10.55				
5	2-Phenyl-(flavanone)	120.87	161.43		138.71	126.07	128.71	128.61
	ΔYb	5.62	2.80		1.19	0.61	0.27	0.25
6	3-Phenyl-(isoflavanone)	121.06	161.56		135.07	127.68	128.80	128.56
7	4*H*-1-Benzothiopyran-4-one Parent	130.74	142.03					
	ΔYb	5.34	2.67					
8	2-Methyl-	130.44	141.60	20.32				
9	3-Methyl-	130.38	141.72	14.86				
10	2-Phenyl-(1-thioflavanone)	130.27	141.95		138.27	127.34	128.86	128.31
	ΔYb	5.02	1.33		1.15	0.55	0.24	0.19
11	3-Phenyl-(1-thioisoflavanone)	131.11	141.66		137.96	128.31	128.44	127.22
12	4*H*-1-Benzothiopyran-4-one 1,1-dioxide Parent	130.50	141.72					
	ΔYb	1.75	1.33					
13	2-Methyl-	130.80	141.06	11.70				
14	3-Methyl-	129.89	141.78	16.56				
15	2-Phenyl-(1-thioflavanone 1,1-dioxide)	130.34	141.29		127.95	128.94	129.76	128.51
	ΔYb	2.37	1.70		0.93	0.31	0.12	0.05
16	3-Phenyl-(1-thioisoflavanone 1,1-dioxide)	130.57	142.18		136.06	128.86	129.29	128.51

a) $Yb(dpm)_3$-induced shift (downfield shift), see experimental section. b) The values in parentheses may be interchanged.

magnitude of the LIS values also supports these signal assignments; the LIS value for the C-4a signal is larger than that for C-8a. Taking into account the substituent parameters of a methyl and an acetyl group on a benzene ring, the resonance of C-7, which is placed at the position *para* to the acetyl group, appears at a field lower than that of C-6, which is in the *meta* position in the chromanone system. The chemical shifts of all the aromatic carbons except C-4a and C-8a are supposed to be in the order of: C-7>C-5>C-6>C-8. The resonances of these carbons demonstrate that the more remote from the carbonyl carbon, the smaller were the LIS usually observed in this system.

For **7**, the resonances of C-4a and C-8a were easily distinguished from those of other aromatic carbons as in the case of the chromanone system. The ^{13}C NMR spectrum of thiophenol indicates that the mesomeric effect of the sulfur atom is smaller on the aromatic ring than that of the oxygen atom: substituted-C, δ 130.80; *o*- or *m*-C, δ 129.28 or 128.92; *p*-C, δ 125.40.[6]

Unlike the case of phenol, the resonance of the *para*-related carbon appeared at a field higher than that of the *ortho*-related carbons. The C-4a signal moved downfield by about 10 ppm, and that for C-8a, upfield by about 20 ppm, compared to those of the corresponding carbons of chromanone. This may be a result of the smaller mesomeric effect of the sulfur atom than that of the oxygen atom. Other aromatic carbon signals are tentatively assigned in taking of the effect of the sulfur atom on the aromatic carbons which appeared in the ^{13}C NMR spectrum of thiophenol. These assignments are supported by their LIS values, much as in the case of the chromanone system.

Since the sulfur atom of the sulfonyl group has no lone-pair electrons, and since this group polarizes as  O^- , this group may act as an electron-attracting group, such as a nitro group. Since the ^{13}C chemical shifts of nitrobenzene are in this order: substituted> *para*->*meta*->*ortho*-related carbons, the resonances at 123—124 and 128—129 are assigned to C-8 and C-5 respectively. The LIS values for these carbons observed in **12** and **15** support these signal assignments. The LIS values suggest that the signals at δ 133.19 and δ 134.90 for **15** correspond to C-6 and C-7 respectively, because carbons which are more remote from the carbonyl group experience smaller shift reagent effects in this system.

Since the resonances of substituted carbons of monoalkylbenzenes are known to occur around δ 140—150, the resonances around δ 140 must correspond to C-1′ in the flavanone system. The resonance of C-1′ of **15** occurs at a field higher than those of other phenyl-substituted compounds. This may be due to the steric γ-gauche interaction with the oxygen atoms of the sulfonyl group, such as the methyl carbon of **13**. When we compare the chemical shifts of alkylbenzenes, the signals of C-2′ and C-6′ or C-3′ and C-5′ may be expected to appear at the same position of the magnetic field, the former carbon atoms appearing at a field slightly higher than those of the latter two.

Experimental

NMR Spectra. The ^{13}C FT-NMR spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 instrument equipped with a JNM-MFT-100 Fourier transform accessory; the instrument was controlled with a JEC-6 spectrum computer. Samples were observed in 5-mm spinning tubes at 20 $\pm 5\%$ solution in $CDCl_3$ at 28 °C. The solvent provided the internal lock signal. The measurement conditions were as follows: pulse width, 27.5 μs (*ca.* 45°); repetition time, 4 s; spectral width, 6250 Hz; data point, 8192; acquisition time, 0.65 s. All the chemical shifts are expressed in δ (ppm downfield from internal Me_4Si). Each observed chemical shift is estimated to be accurate to δ ± 0.06. The LIS values were obtained as follows: each compound (1 mmol) was dissolved in $CDCl_3$ (0.2 ml), and then Yb(dpm)$_3$ (0.15 mmol) was added to the solution, $\Delta Yb=\delta_{Yb}-\delta$.

Materials. The compounds employed in this study have all been previously prepared except **14**: **1**,[7] (bp 82 °C/0.3 mmHg); **2**,[8] (mp 38 °C); **3**,[9] (mp 32 °C); 4,[10] (bp 125—128 °C/11 mmHg); **5**,[11] (mp 76 °C); **6**,[12] (mp 76—77 °C); **7**,[13] (mp 29—30 °C); **8**,[14] (bp 146—147 °C/9 mmHg); **9**,[14] (bp 188—190 °C/12 mmHg); **10**,[15] (mp 55—56 °C); **11**,[16] (bp 170—176 °C/0.5 mmHg); **12**,[17] (mp 131—132 °C); **13**,[18] (mp 138—139 °C); **15**,[18] (mp 133—134 °C); **16**,[16] (mp 151—152 °C). Compound **14** was prepared as follows: 3-methyl-4*H*-1-benzothiopyran-4-one (1 g) in AcOH (10 ml) was treated with H_2O_2 (30%, 2 ml), and then the solution was allowed to stand for 2 days. The product was precipitated by the addition of water. Crystallization from ethanol afforded **14** as colorless prisms; mp 143—145 °C.

References

1) A. Pelter, R. S. Ward, and T. Ian Gray, *J. Chem. Soc. Perkin Trans. 1*, **1976**, 2475, and the references cited therein.

2) F. W. Wehrli, *J. Chem. Soc., Chem. Commun.*, **1975**, 664; H. Wagner, V. M. Chari, and J. Sonnenbichler, *Tetrahedron Lett.*, **1976**, 1799; K. R. Markham and B. Ternai, *Tetrahedron*, **32**, 2607 (1976).

3) R. E. Sievers, "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York (1973).

4) J. A. Hirsch and E. Havinga, *J. Org. Chem.*, **41**, 455 (1976).

5) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Scheli, and D. W. Cookran, *J. Am. Chem. Soc.*, **97**, 322 (1975).

6) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley-Interscience, New York (1972), p. 164.

7) *Org. Synth.*, **35**, 95 (1955).

8) F. Arndt and G. Kallner, *Ber.*, **57**, 202 (1924).

9) G. W. K. Cavill, F. M. Dean, A. McGookin, B. M. Marshall, and A. Robertson, *J. Chem. Soc.*, **1954**, 4573.

10) J. Colonge and A. Guyot, *Bull. Soc. Chim. Fr.*, **1958**, 325.

11) St. V. Kostaneki and W. Szabranski, *Ber.*, **37**, 2634 (1904).

12) N. Inoue, *Nippon Kagaku Zasshi*, **79**, 112 (1958).

13) F. Krollpfeeffer and H. Scheeltze,*Ber.*, **56**, 1819 (1923).

14) J. C. Petropoulos, M. A. McCall, and D. S. Tarbell, *J. Am. Chem. Soc.*, **75**, 1130 (1953).

15) F. Arndt, *Ber.*, **56**, 1269 (1923)

16) G. F. Katebar and R. M. Thomson, *Aust. J. Chem.*, **25**, 647 (1972).

17) F. Arndt, *Ber.*, **58**, 1612 (1925).

18) T. Nambara, Y. Takemori, and S. Okamoto, *Yakugaku Zasshi*, **81**, 1 (1961).