

Carbon-13 Nuclear Magnetic Resonance Spectra of (*Z*)- and (*E*)-Aurones

By Andrew Pelter and Robert S. Ward,* Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

Harry G. Heller, Edward Davies Chemical Laboratory, University College of Wales, Aberystwyth SY23 1NE

The ¹³C n.m.r. spectra of a series of (*Z*)- and (*E*)-aurones have been determined. The differences between the spectra of the (*Z*)- and (*E*)-isomers afford a useful method for distinguishing between the two series.

As a continuation of our investigations of the ¹³C n.m.r. spectra of flavonoids and related compounds,^{1,2} we have studied the spectra of a series of aurones (1)–(18). The

there are reproducible differences between the spectra of the *Z*- and *E*-isomers. The largest differences are observed for the exocyclic olefinic carbon atom (=CH) but

TABLE 1
¹³C Chemical shifts of aurones

Compound	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	=CH	C-2	C-3	C-4	C-5	C-6	C-7	C-7a	C-3a	C-Me	OMe, OAc
(1)	132.25	131.47	128.82	129.81	128.82	131.47	112.88	146.80	184.57	124.55	123.39	136.78	112.88	166.03	121.57		
(2) ^a	137.75	131.13	122.92	147.15	122.92	131.13	108.16	146.97	182.71	123.62	123.53	137.13	112.38	165.05	119.85		55.28
(3)	124.99	133.35	114.43	161.01	114.43	133.35	112.79	145.81	184.31	124.41	123.18	136.43	113.26	165.73	121.89		
(4)	132.42	131.47	128.84	129.72	128.84	131.47	112.50	147.29	184.79	124.23	133.16	137.95	112.50	164.62	121.54	20.73	
(4a)	131.98	130.87	128.45	130.20	128.45	130.87	122.23	148.53	182.82	124.16	132.45	138.00	112.16	163.80	123.31	20.78	
<i>e</i>	-0.44	-0.60	-0.39	+0.48	-0.39	-0.60	+9.73	+1.24	-1.97	-0.07	-0.71	+0.05	-0.34	-0.82	+1.77	+0.05	
(5)	132.63	131.23	128.77	129.37	128.77	131.23	111.27	147.46	184.83	139.52	126.15	148.22	110.16	166.89	117.45	17.69	22.41
(6)	125.39	133.06	114.39	160.70	114.39	133.06	111.64	146.49	184.78	139.41	125.98	147.82	110.14	166.69	117.76	17.72	22.42
(6a)	125.02	132.83	113.81	161.14	113.81	132.83	121.55	147.55	183.02	139.46	125.39	147.82	109.76	165.99	119.35	17.72	22.42
<i>e</i>	-0.37	-0.23	-0.65	+0.44	-0.58	-0.25	+9.91	+1.06	-1.76	+0.05	-0.59	0.00	-0.38	-0.79	+1.59	0.00	0.00
(7)	132.70	131.32	128.82	129.46	128.82	131.32	111.56	147.08	185.88	137.07	124.59	137.13	119.51	164.86	119.11	17.43	13.90
(7a)	132.06	130.73	128.32	129.92	128.32	130.73	121.31	148.18	184.09	137.07	123.88	137.13	119.38	164.22	120.68	17.43	13.73
<i>e</i>	-0.64	-0.59	-0.50	+0.46	-0.50	-0.59	+9.75	+1.10	-1.79	0.00	-0.71	0.00	-0.13	-0.64	+1.57	0.00	-0.17
(8)	131.85	132.58	132.18	129.84	132.18	132.58	110.05	147.50	185.50	137.33	124.90	137.33	119.59	165.01	119.26	17.37	13.85
(8a)	131.00	132.17	131.56	124.21	131.56	132.17	119.88	148.50	184.23	137.25	124.10	137.30	119.44	164.30	120.60	17.46	13.72
<i>e</i>	-0.85	-0.41	-0.62	+0.37	-0.62	-0.41	+9.83	+1.00	-1.27	-0.08	-0.80	-0.03	-0.15	-0.71	+1.34	+0.09	-0.13
(9)	131.22	132.36	129.12	135.36	129.12	132.36	110.06	147.22	185.68	137.12	124.83	137.38	119.54	164.84	119.00	17.42	13.91
(10)	139.22	131.56	124.04	147.51	124.04	131.56	108.10	148.68	185.67	137.69	125.38	137.99	119.71	165.13	118.81	17.50	13.94
(11)	125.34	132.99	114.27	160.59	114.27	132.99	111.65	145.94	185.34	136.58	124.26	136.58	119.30	164.41	119.19	17.29	13.81
(11a)	125.07	132.82	113.69	161.10	113.69	132.82	121.75	147.04	183.58	136.58	123.53	136.58	119.19	163.76	120.79	17.29	13.66
<i>e</i>	-0.27	-0.17	-0.58	+0.51	-0.58	-0.17	+10.10	+1.10	-1.76	0.00	-0.73	0.00	-0.11	-0.65	+1.60	0.00	-0.15
(12)	132.86	131.16	128.73	129.19	128.73	131.16	110.73	146.46	185.35	136.09	126.57	147.62	117.75	165.02	117.09	17.28	20.02
																10.50	
(13)	132.29	131.13	128.66	129.40	128.66	131.13	111.63	147.65	182.67	125.59	112.00	167.22	96.54	168.33	114.69		55.91
(14) ^b	123.41	133.23	116.14	159.30	116.14	133.23	111.93	146.06	182.49	125.25	112.78	166.97	96.46	167.82	114.88		55.92
(15)	130.17	132.48	122.09	151.49	122.09	132.48	110.85	147.77	182.90	125.86	112.28	167.55	96.69	168.57	114.80		56.04
																	21.16
(16) ^c	119.02	157.15	115.60	131.13	119.30	130.93	105.90	146.81	181.77	124.99	111.96	166.87	96.56	167.71	114.41		55.97
(17)	125.00	149.73	122.66	130.24	126.05	131.49	103.99	148.40	182.44	125.75	112.12	167.36	96.58	168.38	114.56		55.96
(18) ^c	128.48	130.21	114.64	157.72	114.64	130.21	127.89	143.12	182.43	124.28	110.98	165.79	95.07	165.99	115.63	14.24	55.1

All spectra run in CDCl₃ except where indicated: ^a (CD₂)₂SO. ^b CDCl₂-(CD₂)₂SO (4 : 1). ^c CDCl₂-(CD₂)₂SO (2 : 1). ^d Confirmed by specific decoupling. Differences between *Z*- and *E*-isomers.

signals (Table 1) were assigned on the basis of their multiplicity in the off-resonance spectra and by consideration of the known substituent effect of the groups concerned.^{3,4} In some cases the assignments were also

carbon atoms 2, 3, and 3a also show significant differences (>1 p.p.m.) between the two isomers (Table 1 and Figure). These differences, particularly in the chemical shift of the olefinic =CH, afford a useful method

TABLE 2
Chemical shifts of *C*-methyl groups of ring A

	Compound									
	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	
4-Me		17.69	17.72 *	17.43 *	17.37	17.26	17.50	17.29	17.28	
5-Me	20.73									
6-Me		22.41	22.42 *							20.02
7-Me				13.90 *	13.85	13.80	13.94	13.81	10.50	

* Confirmed by specific decoupling.

confirmed by specific irradiation at the frequencies of signals in ¹H n.m.r. spectra.

Several features of the spectra are worthy of comment. First, in all cases, except the β-methyl compound (18), the signals due to C-2 and -3 lie within closely defined limits. Thus the carbonyl carbon atom (C-3) absorbs between 181.8 and 185.9 p.p.m. in all the compounds, while the signal for C-2 comes between 145.8 and 148.7 p.p.m. The latter signal appears at 143.1 p.p.m. in the spectrum of the β-methylaurone (18). Secondly,

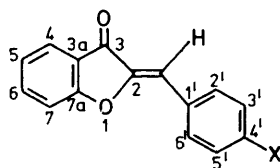
for distinguishing between the two series and represent a considerable improvement over previous methods for assigning the stereochemistry of aurone isomers.⁵ The ¹H n.m.r. spectra, for example, are completely unsatisfactory for this purpose because the olefinic protons have similar chemical shifts in both isomers.

The spectra of compounds (4)–(12) show that the signals due to the *C*-Me groups attached to ring A are characteristic of their position (Table 2).

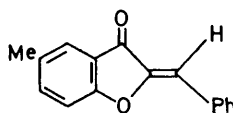
Finally, the substituent effects of groups attached to

ring B are in good agreement with those reported for other benzene derivatives.²⁻⁴ However, introducing a methyl group at C-4 of ring A causes a much greater downfield shift of the C-4 signal itself than would be

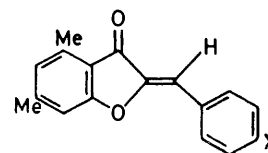
separately at C-6 and C-7 (predicted shifts -0.1 and -2.9).



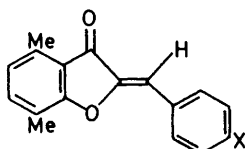
- (1) X = H
 (2) X = NO₂
 (3) X = OMe



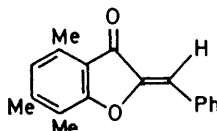
- (4)
 (4a) *E*-isomer



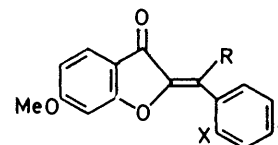
- (5) X = H
 (6) X = OMe
 (6a) *E*-isomer



- (7) X = H
 (7a) *E*-isomer
 (8) X = Br
 (8a) *E*-isomer
 (9) X = Cl
 (10) X = NO₂
 (11) X = OMe
 (11a) *E*-isomer



(12)



- (13) R = X = Y = H
 (14) R = X = H, Y = OH
 (15) R = X = H, Y = OAc
 (16) R = Y = H, X = OH
 (17) R = Y = H, X = OAc
 (18) R = Me, X = H, Y = OH

methyl group at C-4 of ring A causes a much greater downfield shift of the C-4 signal itself than would be

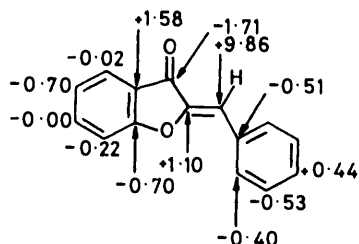
EXPERIMENTAL

The ¹³C spectra were determined using a Varian XL-100 instrument coupled to a 620L-100 computer. Chemical shifts are recorded as p.p.m. downfield from internal tetramethylsilane [solvent CDCl₃ or CDCl₃-(CD₃)₂SO]. The aurones were prepared by known methods.⁵

[8/036 Received, 10th January, 1978]

REFERENCES

- A. Pelter, R. S. Ward, and T. I. Gray, *J.C.S. Perkin I*, 1976, 2475.
- A. Pelter, R. S. Ward, and R. J. Bass, *J.C.S. Perkin I*, 1978, 666.
- G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972.
- J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.
- J. S. Hastings and H. G. Heller, *J.C.S. Perkin I*, 1972, 2128; see also T. J. King, J. S. Hastings, and H. G. Heller, *ibid.*, 1975, 1455.



Mean differences in chemical shift between *Z*- and *E*-isomers

predicted simply on the basis of substituent effects. Thus shifts of $+15.0$ and $+12.9$ p.p.m. occur on introducing methyl groups at the 4,6- and 4,7-positions (predicted shifts $+8.8$ and $+6.0$), and shifts of -1.0 and -3.4 p.p.m. occur on introducing methyl groups