The Stereochemistry of Aurones [2-Substituted Benzylidenebenzofuran-3(2*H*)-ones]

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The stereochemistry of two (*Z*)- and (*E*)-aurones has been established by dipole moment measurements, and a correlation with their characteristic i.r. spectra employed to assign the isomerism in other aurones.

N.m.r. studies on (*Z*)- and (*E*)-aurones are discussed.

In the absence of any data in the literature, the configuration of the aurones has been investigated. As a rule, in αβ-unsaturated carbonyl compounds, the anisotropic, diamagnetic deshielding of the carbonyl group causes the olefinic proton *cis* to the carbonyl to give an absorption at a lower field (*ca.* 1 p.p.m.) than in the *trans* arrangement, so that assignment of configuration can be made on the basis of the chemical shift of the olefinic proton (see Table 1).[1-4] N.m.r. studies on (*Z*)- and (*E*)-aurones show β-hydrogen absorptions at similar chemical shifts (τ 3·0—3·3), so that assignment of configuration based on these signals is inconclusive (see Table 2). The u.v. spectra of (*Z*)- and (*E*)-aurones are too similar to be used to distinguish between isomers.

The stereochemistry has been established by dipole moment measurements on the (*Z*)- and (*E*)-isomers (2

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and 3; X = O, Ar = Ph) and their p-chloro-derivatives (2 and 3; X = O, Ar = p-ClC$_6$H$_4$) in benzene at 25 °C.

TABLE 1

Chemical shifts of olefinic protons in (E)- and (Z)-αβ-unsaturated ketones (τ values)

	τ[(E)-Isomer]	τ [(Z)-Isomer]	Ref.
2-Benzylidene-3,3-diphenylindan-1-one	2·04	3·18	1
2-Benzylidene-3,3-dimethylindan-1-one	2·35	3·20	2
2-Benzylidene-3,4-dihydro-4,4-dimethylnaphthalen-1(2H)-one	2·29	3·37	2
3-Benzylideneflavanone	1·92	3·30	3

Dipole moments were calculated using the Guggenheim equation.[5]

(Z)-2-Benzylidene-4,7-dimethylbenzofuran-3(2H)-one (2; X = O, Ar = Ph) and its p-chloro-derivative (2; X = O, Ar = p-ClC$_6$H$_4$) were prepared by acid-catalysed condensation of 4,7-dimethylbenzofuran-3(2H)-one with benzaldehyde and p-chlorobenzaldehyde, respectively. The (E)-isomers (3; X = O, Ar = Ph and p-ClC$_6$H$_4$) were obtained by irradiation at 366 nm of the respective (Z)-isomer in benzene. Configuration was assigned on the basis that the dipole of the p-chlorophenyl substituent will oppose the group moment of the benzofuranone system in the (Z)-isomer, but reinforce it in the (E)-isomer. That the photoisomers were (E)-aurones and not some other photorearrangement products was demonstrated by quantitative catalytic hydrogenation of both the (Z)-benzylidene-compound (2; X = O, Ar = Ph) and its photoisomer to 2-benzyl-4,7-dimethylbenzofuran-3(2H)-one (4).

Like (E)-2-arylideneindanones[2] (5; X = CH$_2$, R = H), (Z)-aurones (1) show a characteristic medium-to-strong absorption in the i.r. spectrum (1650—1670 cm^{-1}) which is weak or absent in the spectra of their photoisomers (see Table 3 and Figure).[6] I.r. studies on twenty aurones, obtained as the sole products from acid- or base-catalysed condensation of benzofuran-3(2H)-ones with aromatic aldehydes, indicated that only (Z)-isomers were obtained. Some of these aurones have been prepared by different methods[7-10] and can be related to others isolated from flower petals of certain Compositae,[11] indicating that in all cases (Z)-isomers were obtained. (E)-Aurones can be readily obtained in high yield by photoisomerisation of (Z)-isomers.

TABLE 2

N.m.r. data (τ values) on (Z) and (E)-aurones

	=CH	4-Me	6-Me		7-Me	2'- and 6'-H, J_0/Hz[a]
(E)-Isomers						
(3; X = O, Ar = Ph)	3·05	7·35			7·65	1·78q 7
(3; X = O, Ar = p-ClC$_6$H$_4$)	3·13	7·36			7·65	1·85d 9
(6; X = O, R = OMe, Ar = Ph)[b]	3·14					1·85
(6; X = O, R = Me, Ar = Ph)[c]	3·05					1·78q 7
(2; X = CH$_2$, Ar = Ph)[d]	g	7·62			7·30	g
(Z)-Isomers						
(2; X = O, Ar = Ph)	3·21	7·35			7·59	2·10q 7
(2; X = O, Ar = p-ClC$_6$H$_4$)	3·28	7·38			7·58	2·18d 9
(2; X = O, Ar = p-NO$_2$·C$_6$H$_4$)	3·20	7·32			7·52	1·95d 9
(2; X = O, Ar = p-MeO·C$_6$H$_4$)	3·24	7·38			7·60	2·15d 9
(5; X = O, R = OMe, Ar = Ph)[b]	3·20					2·10
(5; X = O, R = Me, Ar = Ph)[c]	3·16					2·08q 7
(1)	3·08					2·08q 7
(1; R$^{4'}$ = Cl)[e]	3·17					2·15d 9
(1; R$^{4'}$ = NO$_2$)	3·11					1·95d 9
(1; R$^{4'}$ = MeO)	3·13					2·08d 9
(1; R^4 = R^6 = R^7 = Me)	3·27	7·40	7·68		7·68	2·10q 7
(1; R$^{4'}$ = R^4 = R^6 = R^7 = Me)	3·30	7·43	7·62	and	7·72	2·24d 9
(1; R$^{2'}$ = R$^{4'}$ = R$^{6'}$ = R^4 = R^6 = R^7 = Me)	3·23	7·35	7·65	and	7·82	
(1; R$^{2'}$ = R$^{6'}$ = Cl, R^4 = R^6 = R^7 = Me)	3·13	7·40	7·68	and	7·83	
(1; R$^{2'}$ = MeO, R^4 = R^6 = R^7 = Me)	3·25	7·36	7·66		7·66	1·66q 7
(1; R$^{3'}$ = R$^{4'}$ = MeO, R^4 = R^6 = R^7 = Me)	3·32	7·42	7·70	and	7·74	2·34d, 2·63q 9
(1; R^4 = R^6 = Me)	3·21	7·35	7·55			2·10q 7
(1; R$^{4'}$ = Cl, R^4 = R^6 = Me)	3·32	7·38	7·58			2·18d 9
(1; R$^{4'}$ = NO$_2$, R^4 = R^6 = Me)	3·23	7·33	7·52			1·95d 9
(1; R$^{4'}$ = MeO, R^4 = R^6 = Me)	3·22	7·35	7·58			2·15d 9
(1; R^4 = R^6 = OH)[f]	3·35					
(1; R$^{3'}$ = R$^{4'}$ = R^4 = R^6 = OH)[f]	3·52					
(3; X = CH$_2$, Ar = Ph)[d]	3·18	7·83			7·40	2·02q 8

[a] J_0 represents $J_{2',3'}$ and/or $J_{5',6'}$. [b] Ref. 12. [c] J. S. Hastings and H. G. Heller, *J.C.S. Perkin I*, 1972, 1839. [d] Note different numbering. [e] In compounds (1), all R = H unless otherwise stated. [f] T. J. Batterham and R. J. Highet, *Austral. J. Chem.*, 1964, **17**, 428. [g] Obscured by other signals.

O'Sullivan and his co-workers[12] have correctly

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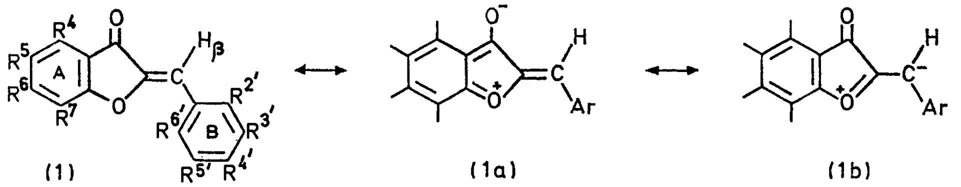
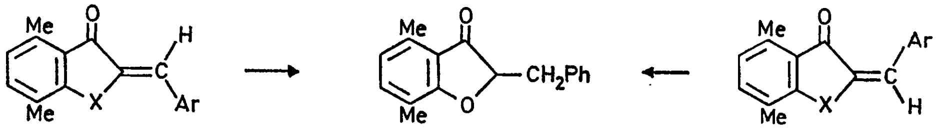
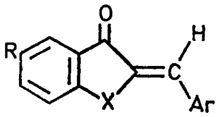
assigned the configuration of aurones on evidence which is, in our opinion, inconclusive. Since configuration could not be assigned on the difference in chemical shift of β-protons in (*Z*)- and (*E*)-aurones, it was made on the difference (0·25 p.p.m.) in chemical shift of the 2′- and 6′-protons in the (*Z*)- and (*E*)-2-benzylidene-5-methoxybenzofuran-3(2*H*)-ones (5 and 6; X = O, R = OMe, Ar = Ph). The photoisomer was assigned the (*E*)-configuration on the basis that the 2′- and 6′-protons would be deshielded by the carbonyl group and would give a signal at lower field (τ 1·85) than in the (*Z*)-isomer. No explanation was offered for the low field absorption at τ 2·1 due to the 2′- and 6′-protons in the (*Z*)-isomer, nor for the observation that the β-proton in the (*E*)-isomer gave an absorption at lower field (τ 3·14) than the (*Z*)-isomer (τ 3·21). The chemical evidence was inconclusive also. Isolation of the (*Z*)-aminobenzylidene-compound (5; X = O, R = H, Ar = *o*-



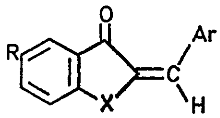
(1) (1a) (1b)



(2) (4) (3)



(5)



(6)

TABLE 3

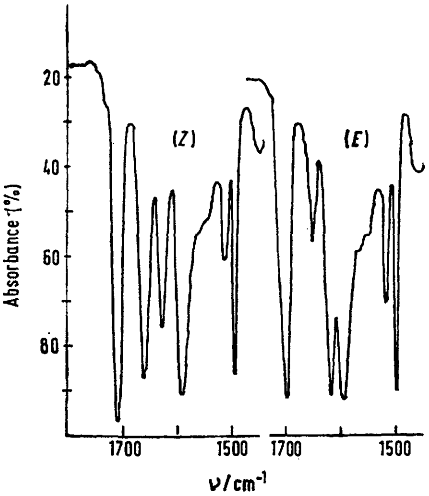
Physical data for the aurones

	Yield (%)	M.p. (°C)	Found (%)		Required (%)		$\nu_{max.}$/cm^{-1} [a]	
			C	H	C	H	(C=O)	(C=C)
(*E*)-Aurones								
(3; X = O, Ar = Ph)	80	85—86	82·0	5·6	81·6	5·6	1683	1650w [b]
(3; X = O, Ar = *p*-ClC_6H_4)	80	143—144	72·0	4·4	71·7	4·6	1700	1650w [b]
(6; X = O, R = Me, Ar = Ph) [e]	80	*d*	81·5	5·1	81·3	5·1	1700	1665w
(*Z*)-Aurones								
(2; X = O, Ar = Ph)	71	112—113	82·1	5·7	81·6	5·6	1696	1656 [b]
(2; X = O, Ar = *p*-ClC_6H_4)	80	199	72·2	4·7	71·7	4·6	1710	1666m [b]
(2; X = O, Ar = *p*-$NO_2{\cdot}C_6H_4$)	82	256—257	69·5	4·6	69·15	4·4	1718	1670
(2; X = O, Ar = *p*-$MeO{\cdot}C_6H_4$)	83	136	77·5	5·8	77·1	5·75	1700	1655
(5; X = O, R = Me, Ar = Ph) [e]	69	117—118	81·5	5·0	81·3	5·1	1710	1660
(1) [e,f]	83	110—111					1712	1660
(1; $R^{4'}$ = Cl) [f]	63	166	70·1	3·5	70·2	3·5	1710	1665
(1; $R^{4'}$ = NO_2) [g]	57	211—212					1720	1668m
(1; $R^{4'}$ = MeO) [h]	69	139					1705	1650
(1; $R^4 = R^6 = R^7$ = Me)	80	185—186					1700	1662
(1; $R^{4'} = R^4 = R^6 = R^7$ = Me)	51	189—190					1695	1655
(1; $R^{2'} = R^{4'} = R^{6'} = R^4 = R^6 = R^7$ = Me)	92	164—165					1710	1670
(1; $R^{2'} = R^{6'}$ = Cl, $R^4 = R^6 = R^7$ = Me)	58	154—155					1700	1665m
(1; $R^{2'}$ = MeO, $R^4 = R^6 = R^7$ = Me)	56	212—213					1695	1655
(1; $R^{3'} = R^{4'}$ = MeO, $R^4 = R^6 = R^7$ = Me)	60	231—232					1690	1650m
(1; $R^4 = R^6$ = Me)	67	169—170					1697	1568
(1; $R^{4'}$ = Cl, $R^4 = R^6$ = Me)	57	164—165	71·7	4·2	71·7	4·6	1700	1660
(1; $R^{4'}$ = NO_2, $R^4 = R^6$ = Me)	74	252—253	69·15	4·55	69·15	4·4	1710	1665
(1; $R^{4'}$ = MeO, $R^4 = R^6$ = Me)	64	156—157	77·5	5·55	77·1	5·75	1700	1660

[a] Strong absorptions unless otherwise stated. [b] Measured for 3% carbon tetrachloride solutions, cell path length 0·5 mm, Nujol mull. [c] Footnote *c* in Table 2. [d] Isomerises on heating above 80—90°. [e] J. Gripenberg, *Acta Chem. Scand.*, 1953, **7**, 1323. [f] See footnote *e* in Table 2. [g] L. Reichel and G. Hempel, *Annalen*, 1959, **625**, 184. [h] K. Auwers and L. Auschütz, *Ber.*, 1921, **54**, 1558, 3331.

$NH_2 \cdot C_6H_4$) from the reduction of the nitro-compound (5 or 6; X = O, R = H, Ar = *o*-$NO_2 \cdot C_6H_4$) with tin(II) chloride and hydrochloric acid does not establish that the nitro-compound was the (*Z*)-isomer. Acid-catalysed isomerisation could have occurred during the reaction as has been demonstrated in related reactions.[3,13,14]

The high field signal of the β-proton in (*Z*)-aurones (1), compared to those in other αβ-unsaturated ketones having the olefinic proton *cis* to the carbonyl group, must be due to the influence of the ring oxygen atom.



I.r. spectra of (*Z*)- and (*E*)-aurones

It is not due to the mesomeric effect shown in the resonance structure (1a) since the deshielding of the carbonyl group on the olefinic proton is not reduced by the ring oxygen atom in 3-arylideneflavanones,[3] and the chemical shift of the 4-methyl group in (*Z*)-benzylidenebenzofuranone (2; X = O, Ar = Ph) (τ 7·35) is similar to that in the corresponding (*E*)-benzylideneindanone (2; X = CH_2, Ar = Ph) (τ 7·30).

Feeney and his co-workers [15] have shown that terminal olefinic protons of vinyl ethers resonate at a higher field (*ca.* 0·75 p.p.m.) than in simple alkenes and that the olefinic proton *trans* to the ether oxygen atom gives a signal at a higher field (*ca.* 0·25 p.p.m.) than in the *cis*-arrangement. It is suggested that the mesomeric effect of the ring oxygen atom shown in structure (1b), causes shielding of the β-protons in (*Z*)- and (*E*)-aurones, thus accounting for the high field signals due to β-protons in the (*Z*)-isomers, and that a lone pair on the ring oxygen atom cause deshielding of the β-protons in the (*E*)-isomers and the 2′- and 6′-protons in (*Z*)-aurones. In *cis*-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-5,9-diol, the aromatic protons show up as an A_2B_2 system centred at τ 2·6 due to the deshielding influence of the equatorial oxygen atoms on the two adjacent aromatic protons.[16] Electron-releasing or -withdrawing substituents in the A or B rings, which should modify the mesomeric effect [see (1b)], cause little change in the chemical shift of the β-, and 2′- and 6′-protons in the (*Z*)-aurones (see Table 2).

EXPERIMENTAL

N.m.r. spectra were obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 spectrometer at 60 MHz with tetramethylsilane as internal standard and i.r. spectra were determined for Nujol mulls unless indicated otherwise with a Perkin-Elmer 237 spectrometer. The permittivities were measured with a W.T.W. Dipolmeter type DMO1.

4,7-*Dimethylbenzofuran*-3(2H)-*one*.[17]— 2,5-Dimethylphenoxyacetyl chloride (20 g) in dry benzene (100 ml) was added rapidly to a well-stirred suspension of anhydrous aluminium chloride (14 g) in benzene (100 ml) and maintained at 5° for 2 h. The mixture was added to crushed ice. Work-up gave the benzofuranone (16·3 g, 91%), m.p. 91—93° (from light petroleum) (lit., 93°), τ 3·27 (1H, d, *J* 7 Hz, 5-H), 3·73 (1H, d, *J* 7 Hz, 6-H), 5·42 (2H, s, CH_2), 7·41 (3H, s, 4-Me), and 7·71 (3H, s, 7-Me).

4,6-*Dimethylbenzofuran*-3(2H)-*one* [17] was prepared in a similar manner in 71% yield, m.p. 72—73° (lit., 73°), τ 3·25 (1H, s, 6-H), 3·32 (1H, s, 5-H), 5·42 (2H, s, CH_2), 7·41 (3H, s, 4-Me), and 7·60 (3H, s, 6-Me).

4,6,7-*Trimethylbenzofuran*-3(2H)-*one*.[18]— 2,3,5-Trimethylphenoxyacetic acid (5 g) was dissolved in conc. sulphuric acid (75 ml), heated to 90°, maintained at this temperature (5 min), and poured carefully onto a minimum of crushed ice. The solid was filtered off, dissolved in ether, and washed with 10% sodium carbonate solution. The ethereal layer was dried and evaporated, and the residue was crystallised from light petroleum, giving the ketone (3·5 g, 78%), m.p. 89—90° (lit., 90·5—91·5), τ 3·31 (1H, s, 5-H), 5·20 (2H, s, CH_2), 7·44 (3H, s, 4-Me), 7·68 (3H, s, 6- or 7-Me), 7·80 (3H, s, 7- or 6-Me).

(Z)-2-*Benzylidene*-4,7-*dimethylbenzofuran*-3(2H)-*one* (2; X = O, Ar = Ph).—Benzaldehyde (3 ml) in ethanol (5 ml) was mixed with 4,7-dimethylbenzofuran-3(2*H*)-one (2·5 g) in ethanol (5 ml) and the solution was heated to 60°. Conc. hydrochloric acid (0·4 ml) was added and the solution was boiled (4 h). On cooling, (Z)-2-*benzylidene*-4,7-*dimethylbenzofuran*-3(2H)-*one* (2·6 g, 67%) crystallised, m.p. 112—113°. The base-catalysed reaction, with 10% w/v ethanolic potassium hydroxide (0·3 ml), gave the (*Z*)-aurone in 35% yield. Only (*Z*)-aurones could be isolated from these reactions. The other (*Z*)-aurones described in Tables 2 and 3 were prepared in a similar manner by acid-catalysed reactions from the appropriate benzofuran-3(2*H*)-one and aromatic aldehyde.

(E)-2-*Benzylidene*-4,7-*dimethylbenzofuran*-3(2H)-*one* (3; X = O, Ar = Ph).—The foregoing (*Z*)-isomer (0·5 g) in benzene (1 l) was exposed to radiation at 366 nm (from four 125 W mercury-discharge lamps with Wood's glass type filters) for 8 h. The solvent was removed and the residue was crystallised from ethanol giving the (E)-*isomer* (0·4 g), m.p. 85—86°.

(E)-2-p-*Chlorobenzylidene*-4,7-*dimethylbenzofuran*-3(2H)-*one* (3; X = O, Ar = *p*-ClC_6H_4) was prepared similarly from the corresponding (*Z*)-isomer.

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2-Benzyl-4,7-dimethylbenzofuran-3(2H)-one (4).—The (*Z*)- or (*E*)-benzofuranone (2 or 3; X = O, Ar = Ph) (0·5 g) in ethanol was hydrogenated at 1 atm over 10% palladium–charcoal. The theoretical amount of hydrogen was absorbed within 1 h. Removal of the catalyst and solvent yielded *2-benzyl-4,7-dimethylbenzofuran-3(2H)-one* in quantitative yield, m.p. 61—62° (from ethanol) (Found: C, 81·3; H, 6·3. $C_{17}H_{16}O_2$ requires C, 80·9; 6·4%), τ 2·68, 2·79 (6H, Ph and 6-H), 3·29 (1H, d, *J* 7 Hz, 5-H), 5·25 (1H, q, *J* 8 and 4 Hz, O·CH), 6·58 (1H, q, *J* 14·5 and 4 Hz, PhC*H*$_2$), 7·17 (1H, q, *J* 14·5 and 8 Hz, PhC*H*$_2$), 7·44 (3H, s, 4-Me), and 7·73 (3H, s, 7-Me).

Determination of Dipole Moments.—The permittivity of a solution is given by $\varepsilon_1 = \varepsilon_0 + k\Delta\Theta$, where ε_0 = permittivity of reference liquid (benzene) and ε_1 = permittivity of the solution, $\Delta\Theta$ is the difference in scale readings when the cell is filled with solution and when it is filled with the reference liquid, and k (the cell constant) = $0{\cdot}922 \times 10^{-3}$; $\Delta = (\varepsilon_1 - \varepsilon_0) = k\Delta\Theta$, and Δ/m is the gradient of line when Δ is plotted against the concentration (m). The dipole moment (μ/D) was calculated by the Guggenheim methods (see Table 4). Changes in refractive index between solvent and solutions produced no significant variation in the calculated dipole moments. The accuracy of the method is within ±1%.

TABLE 4

Compound	$10^{-5}m$/mol ml^{-1}	$10^{-3}\Delta$	$10^{2}\Delta/m$	μ/D
(2; X = O, Ar = Ph)	3·232	45·63	14·09	3·4
	1·616	23·04		
	0·808	9·68		
	0·404	2·34		
(3; X = O, Ar = Ph)	4·80	44·25	7·67	2·5
	2·40	18·17		
	1·20	9·22		
	0·60	5·81		
(2; X = O, Ar = *p*-ClC$_6$H$_4$)	3·688	33·19	8·96	2·7
	1·844	16·78		
	0·922	8·76		
	0·461	3·87		
(3; X = O, Ar = *p*-ClC$_6$H$_4$)	4·26	75·68	18·01	3·8
	2·13	47·94		
	1·06	24·61		
	0·53	12·35		

[2/482 *Received*, 1*st March*, 1972]