X-Ray Analysis of (Z)-2-p-Methoxyphenylmethylenebenzofuran-3(2H)-one

By **Trevor J. King,** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

John S. Hastings and **Harry G. Heller,** * Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 INE

The X-ray structure of the title compound (1 : R = H, Ar = p-MeO·C$_6$H$_4$) establishes that aurones are planar molecules and confirms the (Z)-configuration assigned to naturally occurring and synthetic aurones from a correlation of dipole-moment measurements with their characteristic i.r. spectra.   Crystals are monoclinic, space group P2$_1$/c with a = 12.005(1), b = 3.916(1), c = 27.184(2) Å, β = 106.4°. The structure was solved from diffractometer data by direct methods and refined by block diagonal least-squares methods to R 4.3% for 1875 observed reflections.

(Z)-AURONES, yellow and orange derivatives of 2-aryl-methylenebenzofuran-3(2H)-one, have been isolated from the flower petals of certain Compositae[1] and synthesised by a variety of methods.[2]   Their configur-

ation has been established by dipole-moment measurements on the (Z)- and (E)-aurones [(1) and (2); R = Me,

[1] T. A. Geissman and J. B. Harborne, *J. Amer. Chem. Soc.*, 1956, **78**, 832; S. Arsen and J. R. Plimmer, *Phytochem.*, 1972, **11**, 2601, 2739; E. A. Julian and K. H. Norris, *ibid.*, p. 1841.

[2] T. Emilewicz and St. v. Kostanecki, *Chem. Ber.*, 1899, **32**, 309; K. Auwers and L. Anschutz, *ibid.*, 1921, **54**, 1543; T. S. Wheeler and W. A. Hutchins, *J. Chem. Soc.*, 1939, 91; T. A. Geissman and D. K. Fukushima, *J. Amer. Chem. Soc.*, 1948, **70**, 1686.

Ar = Ph] and their *p*-chloro-derivatives [(1) and (2);
R = Me, Ar = *p*-Cl·C_6H_4] and a correlation with the

(1)   (2)
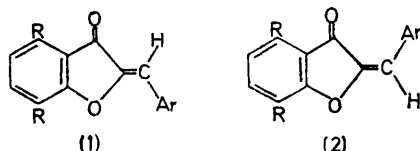
characteristic i.r. spectra of twenty aurones. (*E*)-
Aurones were obtained by photorearrangement of
(*Z*)-isomers.[3]

The u.v. spectra of (*Z*)- and (*E*)-aurones are too
similar to be used to distinguish between isomers and
n.m.r. studies on the isomers showed olefinic absorptions
at similar chemical shifts (τ 3.0—3.3) [3,4] so that assign-
ment of configuration based on these signals is in-
conclusive. As a rule, the anisotropic deshielding of the
carbonyl group causes the olefinic proton *cis* to the
carbonyl to give a signal at lower field (*ca.* 1 p.p.m.)
than in the *trans*-arrangement so that assignment of
configuration of α,β-unsaturated carbonyl compounds is
usually possible on this basis.[5] An explanation for the
anomalous shifts of the olefinic protons in aurones based
on electronic effects has been put forward.[3]

An alternative explanation for the relatively high-
field absorptions of the olefinic protons in (*Z*)-isomers is
that aurones are not rigid planar molecules as suggested
by models but have the 2-arylmethylene group inclined
out of plane of the ring system with the olefinic proton
outside the main deshielding zone of the carbonyl group.

We have, therefore, reinvestigated structure and
stereochemistry by crystallographic methods. The *X*-
ray analysis of *p*-methoxyphenylmethylenebenzofuran-
3(2*H*)-one [(1), R = H, Ar = *p*-MeO·C_6H_4], prepared by
the acid-catalysed condensation of *p*-methoxybenz-
aldehyde with benzofuran-3(2*H*)-one, shows that
aurones are flat molecules, making the foregoing alter-
native explanation for the anomalous chemical shifts of
the olefinic protons untenable, and confirms the (*Z*)-
configuration assigned to naturally occurring and syn-
thetic aurones from a correlation of dipole-moment
measurements and i.r. studies.[3]

EXPERIMENTAL

Crystal Structure Determination.—4′-Methoxyaurone
crystallises from acetic acid as prisms elongated along the
b axis. Oscillation and Weissenberg photographs were
taken about this axis. For intensity measurements a
crystal *ca.* 0.6 × 0.4 × 0.25 mm was mounted about the *b*
axis on a Hilger and Watts four-circle diffractometer. Cell
parameters were refined by a least-squares method using
the positions of 12 reflections and intensity data were
collected (Mo-K_α radiation)by the ω—2θ scan method,
over the range θ 0—30°. The intensities of 3 standard
reflections measured every 100 reflections remained constant
throughout data collection. 1 875 Reflections with a net
count >3σ were considered observed and were used in the
refinement. No absorption corrections were made.

[3] J. S. Hastings and H. G. Heller, *J.C.S. Perkin I*, 1972, 2128.
[4] M. Huke and K. Görlitzer, *Arch. Pharm.*, 1969, **302**, 423.

TABLE 1

Atomic co-ordinates, with standard deviations in
parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
O(1)	0.2189(1)	0.0525(4)	0.0686(1)
C(2)	0.2751(1)	0.2073(5)	0.1068(1)
C(3)	0.2431(1)	0.3086(5)	0.1528(1)
C(4)	0.1419(2)	0.2710(5)	0.1679(1)
C(5)	0.1414(2)	0.4001(6)	0.2149(1)
C(6)	0.2401(2)	0.5581(6)	0.2466(1)
C(7)	0.3413(2)	0.5943(5)	0.2326(1)
C(8)	0.3395(1)	0.4679(5)	0.1850(1)
O(9)	0.4321(1)	0.4845(3)	0.1644(1)
C(10)	0.3965(1)	0.3291(5)	0.1161(1)
C(11)	0.4610(1)	0.2982(5)	0.0839(1)
C(12)	0.5789(1)	0.4040(4)	0.0876(1)
C(13)	0.6232(1)	0.3336(5)	0.0463(1)
C(14)	0.7340(1)	0.4232(5)	0.0406(1)
C(15)	0.8049(1)	0.5888(5)	0.0886(1)
C(16)	0.7639(1)	0.6573(6)	0.1306(1)
C(17)	0.6528(1)	0.5705(5)	0.1302(1)
O(18)	0.9154(1)	0.6949(4)	0.0929(1)
C(19)	0.9612(2)	0.6238(6)	0.0508(1)
H(4)	0.0713(21)	0.1556(64)	0.1451(9)
H(5)	0.0759(17)	0.3785(53)	0.2287(8)
H(6)	0.2370(17)	0.6504(57)	0.2798(9)
H(7)	0.4094(17)	0.7160(54)	0.2554(8)
H(11)	0.4196(16)	0.1790(53)	0.0524(7)
H(13)	0.5789(15)	0.4040(50)	0.8760(7)
H(14)	0.7599(16)	0.3723(49)	0.0162(7)
H(16)	0.8167(17)	0.7702(55)	0.1605(8)
H(17)	0.6248(16)	0.6255(49)	0.1585(7)
H(19A)	1.0369(18)	0.7222(59)	0.0605(8)
H(19B)	0.9634(18)	0.3727(58)	0.0929(8)
H(19C)	0.9106(17)	0.7346(58)	0.0508(8)
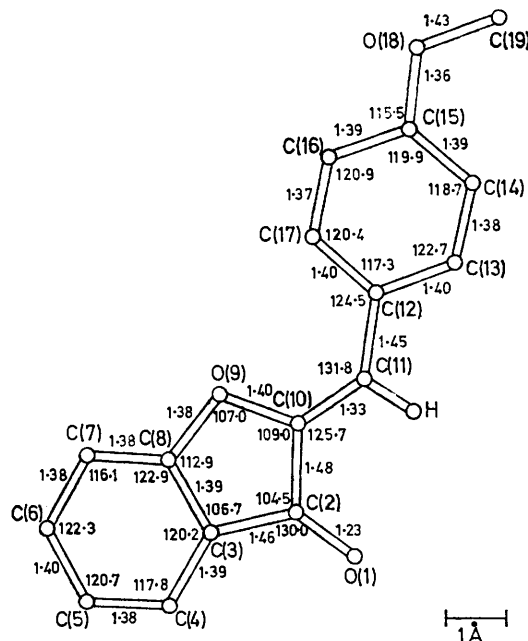
The molecule, showing atom numbering system used in the
analysis, and bond lengths (Å) and angles (deg.)

[5] H. G. Heller and B. Swinney, *J. Chem. Soc.* (C), 1967, 2452;
H. G. Heller and R. M. Megit, *J.C.S. Perkin I*, 1974, 923; D. N.
Kevill, E. D. Weiler, and N. H. Cromwell, *J. Org. Chem.*, 1964,
29, 1276.

$2n + 1$, $h0l$ when $l = 2n + 1$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 1.06 cm^{-1}.

The structure was solved by direct methods by use of the program MULTAN,[6] and the first E map revealed the positions of all but two atoms. Two cycles of block-diagonal least-squares refinement followed by a difference map enabled location of the two remaining atoms. Initially, four cycles of block-diagonal least-squares refinement of atomic positions and isotropic temperature factors were carried out at which stage R was 12%. Two further cycles of anisotropic refinement reduced R to 9.2% and at this stage a difference map revealed the positions of all the hydrogen atoms. A weighting analysis was then carried out and a weighting scheme was adopted of the form: $w = \{1 + [(F_o - B)/A]^2\}^{-1}$, where $A = 9.5$ and $B = 9.0$. After two more cycles of block-diagonal and two cycles of full-matrix refinement with the hydrogen atomic parameters refined isotropically convergence was achieved with a final R of 4.3%. Observed and calculated structure factors, thermal parameters for the non-hydrogen atoms and packing diagrams for the projections along a and b are deposited in Supplementary Publication No. SUP 21313 (11 pp., 1 microfiche).* Final atom positional parameters are listed in the Table.

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

A least-squares planes calculation showed that the molecule is almost completely flat. The maximum deviation (0.1 Å) from the mean plane defined by atoms (1)—(11) being shown by the carbon atom of the methoxy-group. The plane of the benzene ring [atoms (12)—(17)] is twisted with respect to that defined by atoms (1)—(11) by 1.3°.

The Figure shows the molecule with the numbering employed for crystallographic purposes and the bond lengths (mean σ 0.003 Å) and angles (mean σ 0.02°). The C–H bond lengths were all in the range 0.95—1.0 Å with σ *ca.* 0.02 Å.

Intermolecular contact distances were unremarkable except possibly for the relatively close approach (3.3 Å) of the symmetry-related methyl carbon atoms. A packing diagram shows that the methoxy groups point towards each other and the short distance therefore suggests that the hydrogen atoms are interlocked.

Apart for the program MULTAN all computations were carried out by use of the ' X-Ray '70 ' system.[7]

[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.
[7] 1970 revision of ' X-Ray '67,' eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report 67 58, 1967.