2-Methyl-2-(2-methylphenylazo)-1,3-indandione

Süheyla Özbey, Engin Kendi and Semra İde

Department of Physics Engineering,
Faculty of Engineering, Hacettepe University,
06532 Beytepe, Ankara, Turkey

Thomas C. W. Mak

Department of Chemistry, The Chinese University of
Hong Kong, Shatin, New Territories, Hong Kong

Abstract

In the title compound, $C_{17}H_{14}N_2O_2$, the 2-methyl-1,3-dioxoindan-2-yl and 2-methylphenyl groups are *trans* with respect to each other. The phenyl ring and the azo group are not coplanar and have a dihedral angle of 15.4 (2)° between their respective planes. Both benzene ring planes are almost planar within experimental error and the five-membered ring adopts an envelope conformation.

Comment

The study reported here is part of a project aimed at providing a better understanding of the stereochemistry of azo compounds. Azo compounds are used widely in the textile industry as synthetic colouring matters (Venkataraman, 1952). The structure determination of the title compound, (I), was undertaken in order to establish the configuration of the azo group and to compare the values obtained with reported structural results.

(I)
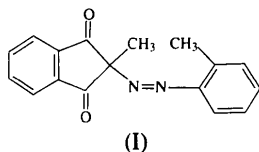
Previous studies involving 2-phenylazo-1,3-indandione and two compounds of the 2-methyl-2-(4-substituted phenylazo)-1,3-indandione series have already been reported (İde, Kendi, Özbey & Ertan, 1994; Özbey, Kendi, Hocaoğlu, Uyar & Mak, 1993; Özbey, Kendi, Hocaoğlu, Uyar, Mak & Cascarano, 1994). The coupling reactions of aromatic diazonium salts with active methinyl compounds are known as Japp–Klingemann reactions and the products are aliphatic carbon–arylazo compounds (Phillips, 1959). 2-Methyl-

2-(2-substituted phenylazo)-1,3-indandiones were obtained by the standard procedure of diazotization of the corresponding substituted anilines and subsequent coupling with 2-methyl-1,3-indandione. 2-Methyl-1,3-indandione was prepared as described in the literature (Wislicenus & Kötzle, 1889). Recrystallization from ethanol gave yellow plate crystals (90–95% yield). The compound was characterized by UV, IR and NMR spectroscopic methods.

We report here the structure of 2-methyl-2-(2-methylphenylazo)-1,3-indandione (I). In the molecule, the 2-methyl-1,3-dioxoindan-2-yl and 2-methylphenyl groups are *trans* with respect to each other, as found in analogous compounds, *e.g.* in 2-(4-chlorophenylazo)-2-methyl-1,3-indandione (Özbey et al., 1993) and 2-methyl-2-(4-nitrophenylazo)-1,3-indandione (Özbey et al., 1994). However, 2-phenylazo-1,3-indandione and its hydrazone form have been found to have a planar conformation in the solid state (İde et al., 1994). Bond lengths and angles of the title molecule agree with the mean values reported for these analogous compounds.
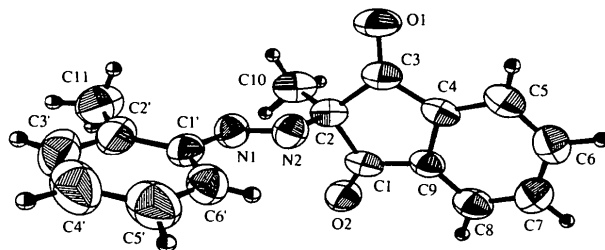

Fig. 1. An *ORTEP*II (Johnson, 1976) view of the molecule showing the numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn with arbitrarily small displacement parameters.

In the phenylazo group the benzene ring plane and the azo group are not coplanar and have a dihedral angle of 15.4 (2)° between the two planes. The angles N2—N1—C1′ and N1—N2—C2 are 114.2 (4) and 113.9 (4)°, respectively; the torsion angle N2—N1—C1′—C2′ is 164.4 (4)° [in 2-phenylazo-1,3-indandione the values of these angles are 120.1 (2), 118.0 (2) and −177.3 (2)°, respectively]. The N=N bond length is 1.221 (4) Å, in accordance with the expected value for aromatic azo compounds. The benzene ring planes in the phenylazo and indandione groups are essentially planar.

The five-membered ring of the indandione moiety has an envelope conformation with the C2 atom 'out-of-plane'. The angle between the least-squares plane through the atoms C3, C4, C9 and C1 and the least-squares plane through C3, C2 and C1 is 13.2 (3)° [13.9 (4)° in 2-(4-chlorophenylazo)-2-methyl-1,3-indandione (Özbey et al., 1993)].

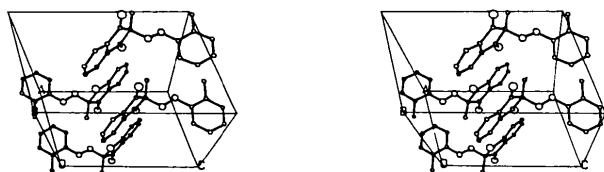|				
C1	0.1308 (6)	0.2032 (3)	0.4055 (4)	0.056 (3)
C2	0.0615 (5)	0.1186 (3)	0.3303 (3)	0.055 (2)
C3	0.1350 (6)	0.0364 (3)	0.4065 (4)	0.059 (3)
C4	0.2679 (6)	0.0724 (3)	0.5040 (4)	0.051 (3)
C9	0.2634 (6)	0.1700 (3)	0.5035 (4)	0.054 (3)
C1'	0.1708 (6)	0.1307 (3)	0.0792 (4)	0.058 (2)
C2'	0.0745 (7)	0.1251 (3)	−0.0296 (4)	0.078 (2)
C5	0.3879 (7)	0.0254 (4)	0.5889 (4)	0.063 (3)
C6	0.5001 (7)	0.0757 (4)	0.6697 (5)	0.073 (3)
C7	0.4913 (7)	0.1728 (4)	0.6695 (5)	0.076 (3)
C8	0.3734 (7)	0.2206 (3)	0.5874 (5)	0.065 (3)
C10	−0.1301 (6)	0.1179 (4)	0.2813 (5)	0.075 (2)
C11	−0.1170 (10)	0.1239 (4)	−0.0637 (6)	0.113 (3)
C3'	0.1678 (13)	0.1172 (4)	−0.1072 (5)	0.104 (4)
C4'	0.3421 (13)	0.1166 (5)	−0.0737 (6)	0.107 (4)
C5'	0.4344 (9)	0.1255 (4)	0.0355 (5)	0.092 (3)
C6'	0.3502 (7)	0.1321 (3)	0.1100 (4)	0.067 (2)

Fig. 2. A stereoscopic packing diagram (*PLUTO*; Motherwell & Clegg, 1978) of the molecule viewed along the *b* axis.

Experimental

The compound was prepared according to the procedure described by Phillips (1959).

Crystal data

C$_{17}$H$_{14}$N$_2$O$_2$
$M_r = 278.3$
Monoclinic
$P2_1/a$
$a = 8.205$ (2) Å
$b = 14.321$ (5) Å
$c = 12.838$ (4) Å
$\beta = 107.73$ (2)°
$V = 1436.9$ (8) Å^3
$Z = 4$
$D_x = 1.287$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 6$–$20°$
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Plate
$0.44 \times 0.44 \times 0.22$ mm
Yellow

Data collection

Nicolet *R*3*m*/*V* diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{min} = 0.959$, $T_{max} = 0.986$
1174 measured reflections
1174 independent reflections

1079 observed reflections
$[F > 4\sigma(F)]$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 13$
2 standard reflections
frequency: 125 min
intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.0529$
$wR = 0.0565$
991 reflections
232 parameters
Only coordinates of H atoms refined

$w = 2.7065/[\sigma^2(F)$
$+ 0.000846F^2]$
$(\Delta/\sigma)_{max} = 0.186$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O2	0.0821 (4)	0.2828 (2)	0.3834 (3)	0.074 (2)
O1	0.0899 (5)	−0.0437 (2)	0.3887 (3)	0.086 (2)
N2	0.1614 (4)	0.1170 (3)	0.2506 (3)	0.060 (1)
N1	0.0758 (4)	0.1331 (2)	0.1564 (3)	0.060 (2)

Table 2. *Selected geometric parameters* (Å, °)

O2—C1	1.212 (5)	C5—C6	1.364 (7)
O1—C3	1.205 (5)	C6—C7	1.392 (8)
N2—N1	1.221 (4)	C7—C8	1.376 (7)
N2—C2	1.493 (6)	C9—C8	1.381 (7)
N1—C1'	1.436 (7)	C1'—C6'	1.403 (7)
C1—C2	1.546 (6)	C2'—C11	1.497 (10)
C1—C9	1.469 (6)	C2'—C3'	1.434 (12)
C2—C3	1.532 (6)	C9—C8	1.381 (7)
C2—C10	1.505 (6)	C3'—C4'	1.362 (14)
C3—C4	1.479 (6)	C4'—C5'	1.382 (9)
C4—C9	1.398 (6)	C5'—C6'	1.343 (10)
C4—C5	1.400 (6)	C1'—C2'	1.382 (6)
N1—N2—C2	113.9 (3)	C4—C5—C6	119.4 (5)
N2—N1—C1'	114.2 (4)	C3—C4—C5	130.8 (4)
O2—C1—C9	127.6 (4)	C3—C4—C9	109.4 (4)
O2—C1—C2	123.9 (4)	C9—C4—C5	119.7 (4)
C2—C1—C9	108.5 (4)	C1—C9—C4	109.8 (4)
N2—C2—C1	105.4 (3)	C4—C9—C8	120.7 (5)
C1—C2—C10	113.9 (4)	C1—C9—C8	129.5 (4)
C1—C2—C3	101.8 (4)	N1—C1'—C6'	123.3 (4)
N2—C2—C10	115.8 (4)	N1—C1'—C2'	115.8 (5)
N2—C2—C3	103.6 (4)	C2'—C1'—C6'	120.9 (5)
C3—C2—C10	114.8 (4)	C1'—C2'—C3'	116.4 (6)
O1—C3—C2	124.9 (4)	C1'—C2'—C11	121.5 (6)
C2—C3—C4	108.5 (4)	C11—C2'—C3'	122.1 (5)
O1—C3—C4	126.6 (6)	C3'—C4'—C5'	121.2 (9)
C5—C6—C7	120.2 (6)	C4'—C5'—C6'	119.2 (7)
C6—C7—C8	121.5 (5)	C1'—C6'—C5'	121.4 (5)
C9—C8—C7	118.4 (5)	C2'—C3'—C4'	120.8 (6)
C2—N2—N1—C1'	−179.4 (4)	C2—C1—C9—C4	−7.9 (5)
N2—N1—C1'—C2'	−14.5 (6)	C1—C9—C4—C3	−0.9 (5)
N2—N1—C1'—C2'	164.4 (4)	C9—C4—C3—C2	9.5 (5)
N1—N2—C2—C1	−113.7 (4)	C4—C3—C2—C1	−13.3 (5)
N1—N2—C2—C3	139.7 (4)	N1—N2—C2—C10	13.2 (5)
C3—C2—C1—C9	12.8 (5)	C6'—C1'—C2'—C11	−179.8 (5)

Data collection, cell refinement and data reduction: Nicolet *R*3*m*/*V* software. Program used to solve structure: *SHELXS*86 (Sheldrick 1990). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978).

References

İde, S., Kendi, E., Özbey, S. & Ertan, N. (1994). *Acta Cryst.* C50, 1505–1507.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.

Özbey, S., Kendi, E., Hocaoğlu, N., Uyar, T. & Mak, T. C. W. (1993). *Acta Cryst.* C49, 2165–2167.

Özbey, S., Kendi, E., Hocaoğlu, N., Uyar, T., Mak, T. C. W. & Cascarano, G. L. (1994). *Acta Cryst.* C50, 629–631.

Phillips, R. R. (1959). *Organic Reactions,* Vol. 10, ch. 2. New York: John Wiley.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Venkataraman, K. (1952). *The Chemistry of Synthetic Dyes,* Vol. 1, p. 703. New York: Academic Press.

Wislicenus, W. & Kötzle, A. (1889). *Ann. Chem.* 252, 72–87.

Antifungal Compounds Isolated from New Zealand Flax: 7-Hydroxy-5-methoxy-6-methylphthalide and 4-Methoxycarbonyl-β-orcinol

GRAEME J. GAINSFORD

*The New Zealand Institute for Industrial Research and Development, PO Box 31-310, Lower Hutt, New Zealand*

Abstract

7-Hydroxy-5-methoxy-6-methylphthalide, $C_{10}H_{10}O_4$, and the β-orcinol compound methyl 2,4-dihydroxy-3,6-dimethylbenzoate, $C_{10}H_{12}O_4$, were obtained from the hexane extracts of air-dried powdered roots of *Phormium cookianum Le Jolis* by column chromatography and repeated recrystallization from hexane/ether solution [Harvey & Waring (1987). *J. Nat. Prod.* 50, 767–776]. X-ray analysis at low temperature (133 K) showed that crystals of the phthalide contain four independent hydrogen-bonded molecules, each of which has one intramolecular hydrogen bond. The five- and six-membered fused rings are planar with an average interplanar angle of 1.9° for three of the molecules, the rings being coplanar in the fourth, which has a weaker intramolecular hydrogen bond. The structure of methyl 2,4-dihydroxy-3,6-dimethylbenzoate at room temperature has been reported previously [Brehm, Stoeckli-Evans, Tabacchi & Bürgi (1983). *Helv. Chim. Acta,* 66,

824–827]. The present low-temperature results are in close agreement with the previous results, the few minor differences being attributable to crystal-packing differences around the ester and hydroxyl groups.

Comment

The two extracts, 7-hydroxy-5-methoxy-6-methylphthalide, (I), and 4-methoxycarbonyl-β-orcinol, (II), from a flax plant, were obtained as part of a concerted study to identify the active ingredients used for curing various ills by New Zealand's Maori people. Neither could be identified uniquely by the usual spectroscopic methods [details of their antifungal properties are reported elsewhere (Harvey & Waring, 1987)].

(I)   (II)
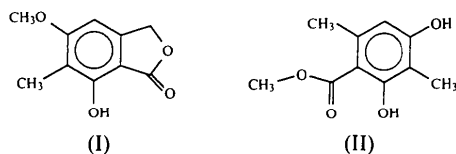
The structure of (I) (Fig. 1) consists of four independent hydrogen-bonded molecules (H···O 2.02–2.29 Å; Table 3). Each of the molecules also has a longer intramolecular hydrogen bond (H···O 2.30–2.69 Å). Comparison of the four molecules confirms the definite planarity of the five- and six-membered rings; the interplanar angles are in the range 1.8–2.0°, except for that of molecule 2, which has a significantly weaker intramolecular hydrogen bond of distorted geometry resulting in the two fused rings being coplanar.

Small but significant deviations from the phthalide ring planes are observed for the carboxyl O [O(n1)] and methyl C atoms [C(n10) and C(n9), where n is the number of the molecule]. Ranges of equivalent bond
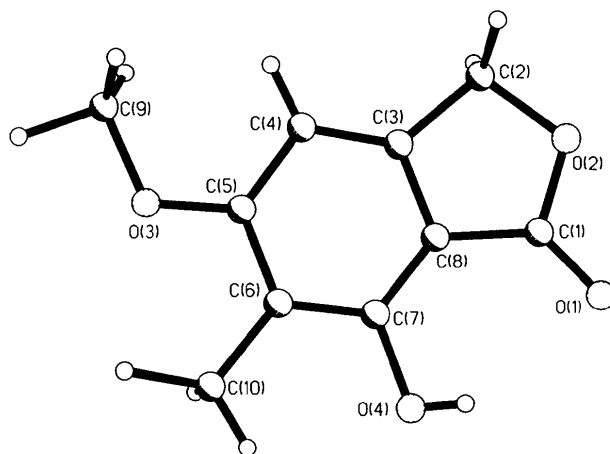

Fig. 1. View of the independent molecule in compound (I) (*SHELXTL;* Sheldrick, 1990). Atom labels in Tables 1 and 2 are based on those shown with a molecule number prefixed, *e.g.* C(21) is atom C(1) in molecule 2.