

$V = 1704.5$  (6) Å<sup>3</sup>  
 $Z = 4$   
*Data collection*  
 Enraf-Nonius Turbo CAD-4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: empirical (Walker & Stuart, 1983)  
 $T_{\min} = 0.72$ ,  $T_{\max} = 1.41$   
 2842 measured reflections  
 2553 independent reflections

$0.5 \times 0.3 \times 0.2$  mm  
 Colourless  
 1227 observed reflections  
 $[I > 2\sigma(I)]$   
 $R_{\text{int}} = 0.031$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = -9 \rightarrow 0$   
 $k = 0 \rightarrow 23$   
 $l = -12 \rightarrow 12$   
 3 standard reflections  
 frequency: 120 min  
 intensity variation: 2.8%

**Refinement**

Refinement on  $F$   
 $R = 0.048$   
 $wR = 0.041$   
 $S = 1.33$   
 1227 reflections  
 190 parameters  
 Only H-atom  $U$ 's refined  
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.01$   
 $\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and the *GX Crystallographic Program System* (Mallinson & Muir, 1985).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Br	0.18821 (11)	0.10429 (4)	-0.08481 (9)	0.054
O(1)	0.1833 (6)	0.5310 (2)	0.6270 (5)	0.049
O(2)	0.4307 (12)	0.4178 (7)	0.5896 (9)	0.151
N(1)	0.2467 (7)	0.3892 (3)	1.0110 (6)	0.033
N(4)	0.2554 (8)	0.3791 (3)	1.2441 (7)	0.046
N(7)	0.1304 (8)	0.2956 (3)	1.0953 (7)	0.043
C(1)	0.1455 (10)	0.3634 (4)	1.1106 (9)	0.040
C(2)	0.4011 (9)	0.4229 (4)	1.1063 (8)	0.044
C(3)	0.3514 (10)	0.4360 (4)	1.2310 (8)	0.051
C(5)	0.3595 (11)	0.3207 (5)	1.3017 (9)	0.062
C(6)	0.2673 (12)	0.2657 (4)	1.2098 (9)	0.064
C(8)	0.1363 (12)	0.2822 (4)	0.9617 (9)	0.063
C(9)	0.2779 (11)	0.3264 (4)	0.9502 (8)	0.048
C(10)	0.1338 (8)	0.4360 (3)	0.9072 (8)	0.038
C(11)	0.2014 (9)	0.4551 (4)	0.7985 (7)	0.039
C(12)	0.1129 (10)	0.5161 (4)	0.7278 (8)	0.043
C(111)	0.1313 (8)	0.5878 (3)	0.5546 (8)	0.040
C(112)	0.2168 (10)	0.6043 (4)	0.4687 (10)	0.048
C(113)	0.1748 (7)	0.6616 (3)	0.3925 (6)	0.056
C(114)	0.0473 (7)	0.7025 (3)	0.4023 (7)	0.058
C(115)	-0.0381 (9)	0.6859 (3)	0.4883 (9)	0.054
C(116)	0.0039 (7)	0.6286 (2)	0.5644 (5)	0.044

Table 2. Geometric parameters (Å, °)

O(1)—C(12)	1.433 (8)	O(1)—C(111)	1.374 (5)
N(1)—C(1)	1.668 (9)	N(1)—C(2)	1.495 (9)
N(1)—C(9)	1.503 (9)	N(1)—C(10)	1.507 (9)
N(4)—C(1)	1.419 (9)	N(4)—C(3)	1.452 (9)
N(4)—C(5)	1.477 (10)	N(7)—C(1)	1.398 (9)
N(7)—C(6)	1.469 (10)	N(7)—C(8)	1.463 (10)
C(2)—C(3)	1.550 (11)	C(5)—C(6)	1.505 (11)
C(8)—C(9)	1.537 (11)	C(10)—C(11)	1.513 (10)
C(11)—C(12)	1.508 (10)		

C(12)—O(1)—C(111)	117.5 (5)	C(1)—N(1)—C(2)	103.8 (6)
C(1)—N(1)—C(9)	102.3 (6)	C(1)—N(1)—C(10)	109.3 (5)
C(2)—N(1)—C(9)	116.1 (6)	C(2)—N(1)—C(10)	111.3 (6)
C(9)—N(1)—C(10)	113.1 (6)	C(1)—N(4)—C(3)	105.6 (7)
C(1)—N(4)—C(5)	107.7 (7)	C(3)—N(4)—C(5)	114.8 (7)
C(1)—N(7)—C(6)	107.8 (7)	C(1)—N(7)—C(8)	105.3 (7)
C(6)—N(7)—C(8)	115.5 (7)	N(1)—C(1)—N(4)	105.2 (6)
N(1)—C(1)—N(7)	106.6 (6)	N(4)—C(1)—N(7)	109.8 (7)
N(1)—C(2)—C(3)	102.5 (6)	N(4)—C(3)—C(2)	106.2 (7)
N(4)—C(5)—C(6)	104.3 (7)	N(7)—C(6)—C(5)	106.8 (7)
N(7)—C(8)—C(9)	105.6 (7)	N(1)—C(9)—C(8)	101.9 (6)
N(1)—C(10)—C(11)	114.1 (6)	C(10)—C(11)—C(12)	109.7 (7)
O(1)—C(12)—C(11)	106.4 (7)	O(1)—C(111)—C(112)	115.8 (3)
O(1)—C(111)—C(116)	124.2 (3)		

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71368 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1050]

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## 2-(4-Chlorophenylazo)-2-methyl-1,3-indandione

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**Abstract**

In the title compound, C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>2</sub>, the 2-methyl-1,3-dioxindan-2-yl and 4-chlorophenyl groups are *trans* to each other. The five-membered ring of the

indandione moiety adopts an envelope conformation. The phenyl and azo groups are not coplanar because of steric hindrance between the lone-pair orbitals on the carbonyl O atom and  $\beta$ -N atom [C—N=N = 112.4 (3)°].

### Comment

The work reported here is part of a project aimed at providing a better understanding of the stereochemistry of azo compounds. The structure determination of the title compound was undertaken to establish whether the indandione moiety would be formed *cis* or *trans* to the 4-chlorophenyl group. Details of the synthetic work will be published elsewhere (Hocaoglu, 1993).

In the title compound the 2-methyl-1,3-dioxindan-2-yl and 4-chlorophenyl groups are *trans*. The five-membered ring of the indandione moiety is in an envelope conformation with C2 the out-of-plane atom. The angle between the least-squares planes through atoms C3, C4, C9 and C1, and C3, C2 and C1 is 13.9 (4)°. Endocyclic torsion angles (starting with C3—C2—C1—C9 and proceeding around the ring) are 13.0 (4), -9.5 (4), 1.2 (5), 7.6 (4) and -12.5 (4)°, respectively.

The benzene rings with the attached H atoms are planar but H3' and H5' are slightly displaced from the benzene plane because of the steric bulk of the Cl atom. The angles C4'—C3'—H3' and C4'—C5'—H5' are 115 (2) and 116 (2)°, respectively. The N=N bond length is 1.231 (4) Å in accordance with the expected value for aromatic azo compounds.

In the phenylazo group the observed bond lengths and angles deviate significantly from corresponding values found for the aliphatic azo compounds. The angles N2—N1—C1' and N1—N2—C2 are 112.4 (3) and 113.5 (3)°, respectively; torsion angles N2—N1—C1'—C6' and N2—N1—C1'—C2' are 11.9 (6) and -169.1 (4)°, respectively. Thus the benzene ring skeleton and the azo group are not coplanar.

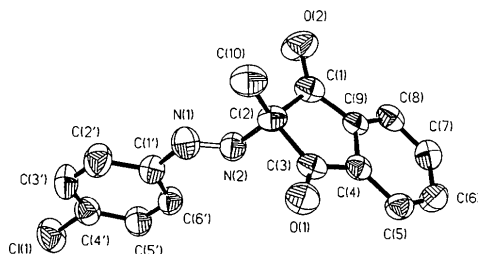


Fig. 1. Perspective view of the molecular structure with atom labelling. The atoms are shown as 50% thermal ellipsoids and the N=N bond is represented by an open line.

The present results show that the azo group is nonplanar because of steric repulsion between the lone-pair orbitals of the carbonyl O atom and the  $\beta$ -N atom.

### Experimental

#### Crystal data

C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 298.728  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 12.424 (2) Å  
*b* = 14.402 (2) Å  
*c* = 8.090 (1) Å  
 $\beta$  = 101.06°  
*V* = 1420.66 (35) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.397 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\lambda$  = 0.7107 Å  
 Cell parameters from 15 reflections  
 $\theta$  = 6–20°  
 $\mu$  = 0.27 mm<sup>-1</sup>  
*T* = 293 K  
 Plate  
 0.3 × 0.3 × 0.2 mm  
 Yellow

#### Data collection

Nicolet R3m/V diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: empirical  
*T<sub>min</sub>* = 0.825, *T<sub>max</sub>* = 0.892  
 1439 independent reflections

1345 observed reflections  
 $[F_o > 4\sigma(F_o)]$   
 $\theta_{\max}$  = 24°  
*h* = -14 → 14  
*k* = 0 → 16  
*l* = 0 → 9  
 2 standard reflections  
 frequency: 125 min  
 intensity variation: 0.9%

#### Refinement

Refinement on *F*  
*R* = 0.037  
*wR* = 0.037  
 1259 reflections  
 $[F > 5\sigma(F)]$   
 224 parameters  
 Only coordinates of H atoms refined  
 Unit weights applied

$(\Delta/\sigma)_{\max}$  = 0.027  
 $\Delta\rho_{\max}$  = 0.095 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.097 e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Since difference synthesis did not clearly show the positions of the H atoms, they were placed in calculated positions and refined with a common temperature factor. Refinement was by full-matrix least-squares methods. Data collection, cell refinement and data reduction: Nicolet R3m/V software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1987). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Cl	1.1521 (1)	0.3762 (1)	1.0029 (2)	0.0820 (6)
O1	0.6069 (3)	0.2181 (2)	0.1805 (4)	0.0615 (15)
O2	0.6001 (3)	0.5432 (2)	0.1876 (5)	0.0749 (15)

N2	0.7371 (2)	0.3820 (2)	0.3688 (4)	0.0512 (14)
N1	0.8337 (2)	0.3716 (3)	0.3570 (4)	0.0568 (15)
C3	0.5845 (3)	0.2969 (2)	0.2128 (6)	0.0431 (19)
C2	0.6596 (3)	0.3814 (3)	0.2030 (6)	0.0421 (18)
C9	0.4841 (3)	0.4262 (2)	0.2746 (5)	0.0397 (19)
C1	0.5816 (4)	0.4634 (2)	0.2185 (6)	0.0474 (22)
C4	0.4854 (3)	0.3297 (3)	0.2692 (5)	0.0398 (20)
C4'	1.0580 (3)	0.3744 (3)	0.8147 (7)	0.0550 (22)
C1'	0.9064 (3)	0.3713 (3)	0.5187 (7)	0.0464 (25)
C7	0.3191 (4)	0.4225 (3)	0.3785 (6)	0.0578 (22)
C8	0.4000 (4)	0.4742 (3)	0.3290 (6)	0.0497 (21)
C6	0.3202 (4)	0.3259 (3)	0.3721 (7)	0.0595 (24)
C5	0.4022 (4)	0.2780 (3)	0.3175 (6)	0.0495 (20)
C10	0.7077 (4)	0.3827 (4)	0.0479 (7)	0.0612 (25)
C6'	0.8727 (3)	0.3651 (3)	0.6692 (7)	0.0540 (25)
C3'	1.0929 (3)	0.3783 (4)	0.6654 (8)	0.0694 (25)
C2'	1.0175 (3)	0.3763 (4)	0.5168 (7)	0.0671 (23)
C5'	0.9476 (3)	0.3662 (4)	0.8195 (6)	0.0599 (21)

Table 2. Geometric parameters (Å, °)

Cl—C4'	1.733 (5)	C9—C8	1.393 (6)
O1—C3	1.209 (4)	C4—C5	1.389 (6)
O2—C1	1.208 (4)	C4'—C3'	1.360 (5)
N2—N1	1.231 (4)	C4'—C5'	1.385 (5)
N2—C2	1.494 (4)	C1'—C6'	1.364 (5)
N1—C1'	1.440 (5)	C1'—C2'	1.385 (5)
C3—C2	1.545 (5)	C7—C8	1.371 (6)
C3—C4	1.471 (6)	C7—C6	1.392 (5)
C2—C1	1.548 (6)	C6—C5	1.372 (6)
C2—C10	1.489 (6)	C6'—C5'	1.382 (5)
C9—C1	1.474 (6)	C3'—C2'	1.375 (6)
C9—C4	1.391 (4)		
N1—N2—C2	113.5 (3)	C1—C9—C8	128.9 (3)
N2—N1—C1'	112.4 (3)	C1—C9—C4	109.8 (3)
O1—C3—C4	127.6 (3)	C2—C1—C9	108.2 (3)
O1—C3—C2	124.2 (3)	O2—C1—C9	127.6 (3)
C2—C3—C4	108.2 (3)	O2—C1—C2	124.2 (4)
N2—C2—C3	104.5 (3)	C3—C4—C9	110.3 (3)
C3—C2—C10	113.4 (4)	C9—C4—C5	120.9 (4)
C3—C2—C1	101.7 (3)	C3—C4—C5	128.9 (4)
N2—C2—C10	117.6 (4)	Cl—C4'—C5'	118.8 (4)
N2—C2—C1	103.2 (3)	Cl—C4'—C3'	120.2 (3)
C1—C2—C10	114.7 (4)	C3'—C4'—C5'	120.9 (5)
C4—C9—C8	121.3 (3)	N1—C1'—C2'	116.3 (5)
N1—C1'—C6'	124.3 (4)	C4—C5—C6	117.4 (4)
C6'—C1'—C2'	119.4 (5)	C1'—C6'—C5'	120.9 (4)
C8—C7—C6	121.3 (5)	C4'—C3'—C2'	119.7 (4)
C9—C8—C7	117.3 (4)	C1'—C2'—C3'	120.3 (4)
C7—C6—C5	121.8 (4)	C4'—C5'—C6'	118.7 (4)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71376 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1072]

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## Structure of 3-Benzyl-2-(3-hydroxy-2-pyridylimino)-4-methyl-2,3-dihydro-1,3-thiazole, † C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>OS

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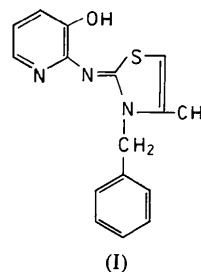
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## Abstract

The hydroxyl H atom takes part in a bifurcated hydrogen bond. The strong intramolecular O—H···N<sub>imino</sub> bond is complemented by the weak O—H···O bond [O···O 3.023 (3), H···O 2.58 (3) Å, O—H···O 113 (2)°], which is responsible for the coupling of the molecules in centrosymmetric dimers. The bifurcation angle N···H···O is 100 (1)°. The molecular dimers are held together only by van der Waals forces.

## Comment

The synthetic route for functionalized thiadiazines and thiazolimines was reported recently by Tosheva & Kalcheva (1993). Ring transformations of oxazoles into analogous derivatives have been discussed previously (Sasaki, Ito & Shimizu, 1982).



In the title compound (I), the thiazole ring is planar to within 0.004 (3) Å and the interatomic distances in the ring indicate double-bond character for C2—C3 [1.332 (5) Å]. The lengths of S—C1 [1.762 (4) Å] and S—C3 [1.749 (3) Å] fall within the range of an S—C<sub>sp</sub><sup>2</sup> single bond [1.751 (17) Å; Allen *et al.*, 1987]. The C1—

† 2-(3-Benzyl-4-methyl-2,3-dihydro-1,3-thiazol-2-ylideneamino)-pyridin-2-ol.