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

	(*A*)	(*B*)
O13—C12	1.331 (2)	1.321 (2)
O13—C14	1.454 (3)	1.446 (2)
O15—C12	1.194 (2)	1.206 (2)
O17—C16	1.329 (2)	1.327 (2)
O17—C18	1.449 (3)	1.452 (2)
O19—C16	1.204 (2)	1.195 (2)
N1—N2	1.357 (2)	1.358 (2)
N1—C5	1.487 (2)	1.480 (2)
N1—C6	1.399 (2)	1.401 (2)
N2—C3	1.284 (2)	1.281 (2)
N21—C20	1.184 (3)	1.197 (3)
C3—C4	1.491 (2)	1.488 (3)
C3—C16	1.461 (2)	1.460 (2)
C4—C5	1.534 (2)	1.532 (2)
C5—C20	1.440 (2)	1.435 (2)
C7—C12	1.487 (3)	1.487 (2)
C12—O13—C14	115.8 (2)	117.9 (2)
C16—O17—C18	117.1 (2)	116.7 (2)
C5—N1—C6	125.3 (2)	126.0 (2)
N2—N1—C6	119.8 (2)	119.9 (2)
N2—N1—C5	112.3 (2)	111.5 (2)
N1—N2—C3	109.5 (2)	108.8 (2)
N2—C3—C16	122.1 (2)	124.0 (2)
N2—C3—C4	113.9 (2)	113.9 (2)
C4—C3—C16	123.9 (2)	122.0 (2)
C3—C4—C5	102.4 (2)	101.1 (2)
N1—C5—C4	101.7 (2)	101.0 (2)
C4—C5—C20	114.1 (2)	114.3 (2)
N1—C5—C20	110.8 (2)	112.7 (2)
N1—C6—C11	120.2 (2)	118.9 (2)
N1—C6—C7	120.9 (2)	121.0 (2)
C6—C7—C12	123.9 (2)	123.2 (2)
C8—C7—C12	117.2 (2)	118.1 (2)
O15—C12—C7	124.0 (2)	124.3 (2)
O13—C12—C7	112.5 (2)	112.5 (2)
O13—C12—O15	123.3 (3)	123.1 (2)
O19—C16—C3	122.6 (2)	121.9 (2)
O17—C16—C3	113.0 (2)	114.9 (2)
O17—C16—O19	124.4 (2)	123.1 (2)
N21—C20—C5	178.1 (3)	177.4 (2)
N1—N2—C3—C4	3.52 (3)	−2.22 (3)
N2—C3—C4—C5	−2.09 (2)	13.27 (3)
C3—C4—C5—N1	−0.07 (2)	−17.30 (2)
C4—C5—N1—N2	2.08 (2)	18.19 (2)
C5—N1—N2—C3	−3.55 (2)	−10.83 (2)
N2—N1—C6—C7	−19.52 (3)	−33.35 (3)
C6—C7—C12—O13	−61.22 (3)	−52.96 (3)
N2—C3—C16—O17	5.06 (3)	−0.12 (3)

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction: *SDP* (Frenz, 1983). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983*a*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Phenylhydrazone Form of 2-Phenylazo-1,3-indandione

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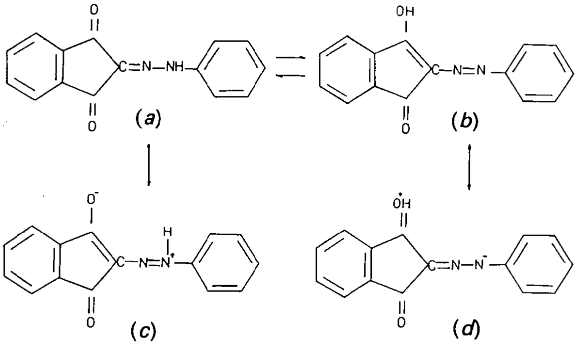
Abstract

In the solid state, 2-phenylazo-1,3-indandione, $C_{15}H_{10}N_2O_2$, exists as a keto–hydrazone tautomer 2-phenylhydrazono-1,3-indandione. The bond distance of one of the keto groups, is slightly elongated [1.230 (3) *cf.* 1.217 (2) Å] as a result of resonance. This resonance is also indicated by an averaging of the single and double bonds in the crystal structure. A strong intramolecular hydrogen bond is found between the elongated oxo group and the amine H atom.

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 molecule has the hydrazone or azo form. 2-Phenylazo-1,3-indandione was first synthesized and characterized by UV, IR, NMR and mass spectroscopy by Hocaoğlu, Uyar & Türker (1990). The compound was obtained through Japp–Kligemann reactions from 2-acetyl-1,3-indandione (at C2) and aniline, then recrystallized in ethanol; m.p. 465–467 K. 2-(2-Methylphenylazo)-1,3-indandione and two compounds in the 2-methyl-2-substituted phenylazo-1,3-indandione series have already been studied (İde, Kendi & Ertan, 1994; Özbey, Kendi, Hocaoğlu, Uyar & Mak, 1993; Özbey, Kendi, Hocaoğlu, Uyar, Mak & Cascarano, 1994). The five-membered ring of the indandione moiety in the 2-methyl-2-substituted phenylazo compounds adopts an envelope conformation; in the title compound, a slight envelope conformation is found for the five-membered ring [C9—C4—C3—C2 = −2.6 (2), C4—C3—C2—C1 = 2.2 (2)°]. In the phenylazo group of the molecule the benzene-ring plane and hydrazone group deviate from coplanarity [N1—N2—C10—C11 = −177.3 (2), N2—N1—C2—C1 = −179.5 (2)°]. The molecule exhibits a slightly distorted planar conformation.

The bond lengths indicating the hydrazone–azo tautomerism are C3—C2 = 1.466 (2), C3=O1 = 1.230 (3), C2=N1 = 1.316 (2), N1—N2 = 1.303 (3) and N2—H = 0.95 (2) Å. The C2=N1 and N1—N2 bond lengths differ from the expected values of 1.36–1.39 Å and 1.33–1.38 Å for C—N and N—N single bonds, respectively, and of 1.27–1.29 Å and 1.23–1.28 Å for C=N and N=N double bonds, respectively. The above observations suggest resonance within the indandione group in conjugation with the phenylazo group. The C2=N1 and N1—N2 bond lengths may differ from the expected values as a result of electron-density replacement. In the keto–hydrazone and the azo–enol tautomers, the resonance effect is illustrated in the scheme below, where (*a*) is the hydrazone and (*b*) the azo form, while (*c*) and (*d*) show the corresponding resonance hybrids.



An important feature of the molecule is the strong intramolecular bond formed between the 3-oxo group and the amine H atom [NH···O = 2.08 (2) Å]. Experimental and theoretical studies of ground and excited states in molecules containing the azo–hydrazone tautomerism have shown that the hydrazone form is more stable than the azo form (Bigelow, 1979; Pendergrass, Paul & Curtin, 1972). The present work indicates that $C_{15}H_{10}N_2O_2$ also has the hydrazone form in the solid state.

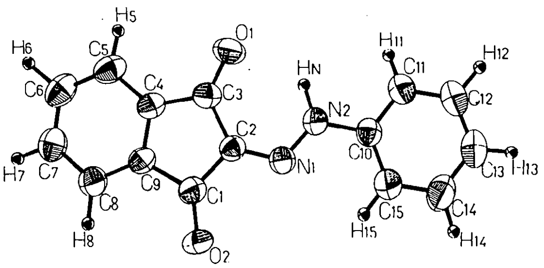


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule with 50% probability ellipsoids and the atom-numbering system. H atoms are shown as circles of arbitrary radii.

Experimental

Crystal data

$C_{15}H_{10}N_2O_2$
$M_r = 250.26$
Monoclinic
$P2_1/c$
$a = 4.523$ (1) Å
$b = 18.870$ (1) Å
$c = 14.205$ (1) Å
$\beta = 91.134$ (9)°
$V = 1212.3$ (2) Å^3
$Z = 4$
$D_x = 1.3713$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 100 reflections
$\theta = 40.0$–47.0°
$\mu = 0.722$ mm^{-1}
$T = 293$ (1) K
Needle
0.4 × 0.3 × 0.25 mm
Orange

Data collection

CAD-4 Mach/Express diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.626$, $T_{\max} = 0.983$
2792 measured reflections
2158 independent reflections
2064 observed reflections [$F > 4\sigma(F)$]

$R_{\text{int}} = 0.05$ for 385 reflections
$\theta_{\max} = 74.3$°
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 96 reflections intensity variation: 3.3%

Refinement

Refinement on F
$R = 0.0532$
$wR = 0.0520$
$S = 0$
1979 reflections
211 parameters
All H-atom parameters refined
$w = 1.4001/[\sigma^2(F_o) + 0.00001(F_o)^2]$

$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.205$ e Å^{-3}
$\Delta\rho_{\min} = -0.224$ e Å^{-3}
Extinction correction: *SHELX*76 (Sheldrick, 1976)
Atomic scattering factors from *SHELXS*86 (Sheldrick, 1985)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.3049 (3)	0.6303 (1)	0.3089 (1)	0.0493 (5)
N2	0.1935 (3)	0.5713 (1)	0.3400 (1)	0.0515 (5)
O1	0.5595 (3)	0.5895 (1)	0.4994 (1)	0.0694 (5)
O2	0.5984 (3)	0.7635 (1)	0.2608 (1)	0.0707 (5)
C1	0.6393 (4)	0.7302 (1)	0.3333 (1)	0.0485 (6)
C2	0.5031 (4)	0.6630 (1)	0.3622 (1)	0.0457 (6)
C3	0.6204 (4)	0.6436 (1)	0.4556 (1)	0.0490 (6)
C4	0.8215 (4)	0.7014 (1)	0.4852 (1)	0.0457 (6)
C5	0.9816 (5)	0.7109 (1)	0.5690 (1)	0.0593 (7)
C6	1.1559 (5)	0.7706 (1)	0.5777 (2)	0.0665 (8)
C7	1.1722 (5)	0.8194 (1)	0.5054 (2)	0.0641 (8)
C8	1.0124 (4)	0.8110 (1)	0.4219 (2)	0.0547 (7)
C9	0.8380 (4)	0.7515 (1)	0.4129 (1)	0.0452 (6)
C10	−0.0163 (4)	0.5336 (1)	0.2845 (1)	0.0487 (6)
C11	−0.1370 (5)	0.4728 (1)	0.3227 (2)	0.0604 (7)
C12	−0.3391 (5)	0.4341 (1)	0.2706 (2)	0.0687 (8)
C13	−0.4220 (5)	0.4554 (1)	0.1816 (2)	0.0691 (8)
C14	−0.3017 (5)	0.5161 (1)	0.1441 (2)	0.0713 (9)
C15	−0.0988 (4)	0.5562 (1)	0.1958 (2)	0.0600 (7)

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

N1—N2	1.303 (3)	C5—C6	1.379 (3)
N1—C2	1.316 (2)	C6—C7	1.383 (4)
N2—C10	1.414 (2)	C7—C8	1.386 (4)
O1—C3	1.230 (3)	C8—C9	1.377 (3)
O2—C1	1.217 (2)	C10—C11	1.386 (3)
C1—C2	1.472 (3)	C10—C15	1.375 (3)
C1—C9	1.486 (2)	C11—C12	1.375 (3)
C2—C3	1.466 (2)	C12—C13	1.372 (4)
C3—C4	1.476 (3)	C13—C14	1.380 (3)
C4—C5	1.393 (2)	C14—C15	1.388 (3)
C4—C9	1.399 (2)		
N2—N1—C2	118.0 (2)	C5—C6—C7	121.1 (2)
N1—N2—C10	120.1 (2)	C6—C7—C8	121.7 (2)
O2—C1—C2	128.6 (2)	C7—C8—C9	117.5 (2)
O2—C1—C9	125.7 (2)	C1—C9—C8	128.9 (2)
C2—C1—C9	105.7 (1)	C4—C9—C8	121.5 (2)
N1—C2—C1	121.9 (1)	C1—C9—C4	109.6 (2)
N1—C2—C3	129.4 (2)	N2—C10—C15	121.5 (2)
C1—C2—C3	108.8 (1)	N2—C10—C11	117.6 (2)
O1—C3—C2	125.8 (2)	C11—C10—C15	120.9 (2)
O1—C3—C4	127.8 (2)	C10—C11—C12	119.5 (2)
C2—C3—C4	106.5 (2)	C11—C12—C13	120.5 (2)
C3—C4—C5	130.2 (2)	C12—C13—C14	119.8 (2)
C3—C4—C9	109.4 (1)	C13—C14—C15	120.7 (2)
C5—C4—C9	120.4 (2)	C10—C15—C14	118.7 (2)
C4—C5—C6	117.9 (2)		

All H atoms were located unambiguously in $\Delta\rho$ maps and refined with isotropic displacement parameters. Programs used for data collection, cell refinement and data reduction: Enraf–Nonius CAD-4 software. Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983). Program used for molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of (1) *N*-(2-Pyridyl)-, (2) *N*-(3-Pyridyl)- and (3) *N*-(4-Pyridyl)-*N*′-(4-chlorophenyl)urea

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Abstract

The three compounds ($C_{12}H_{10}ClN_3O$) have similar molecular structures but differ in the position of the N atom in the pyridyl ring. The effects are reflected in the existence of some intra- or intermolecular hydrogen bonds between the urea N atoms and the pyridyl N atom {1.89 (4) [(1) intra], 2.21 (3) and 2.14 (3) [(2) inter], 2.17 (2) [(3) inter]} and between the carbonyl O and the pyridyl N atom {2.07 (4) Å [(1) inter]}. From the intermolecular distances the crystal structure of (1) can be viewed as a succession of 'dimers' in three dimensions, and that of (2) or (3) as a one-dimensional molecular chain.

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