

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B _{eq}
S	0.9290 (1)	0.0650 (5)	0.2657 (1)	4.80 (5)
O1	0.7810 (3)	0.774 (1)	0.3682 (3)	4.6 (1)
O2	0.8924 (3)	0.734 (1)	0.4802 (3)	5.0 (1)
O3	0.7767 (3)	0.933 (1)	0.5532 (3)	4.6 (1)
O4	0.5765 (3)	0.978 (1)	0.4563 (3)	5.0 (1)
O5	0.5577 (3)	1.277 (1)	0.5353 (3)	4.5 (1)
N1	0.8316 (3)	0.416 (1)	0.2826 (3)	3.8 (1)
N2	0.9475 (3)	0.349 (1)	0.3957 (3)	3.5 (1)
C1	0.9021 (4)	0.294 (1)	0.3208 (4)	3.0 (2)
C2	1.0326 (4)	-0.038 (2)	0.3327 (4)	3.8 (2)
C3	1.0759 (4)	-0.199 (1)	0.2861 (4)	3.1 (2)
C4	1.1180 (5)	-0.404 (1)	0.3234 (4)	3.5 (2)
C5	1.1623 (4)	-0.547 (2)	0.2858 (4)	4.1 (2)
C6	1.1645 (5)	-0.479 (2)	0.2090 (4)	4.2 (2)
C7	1.1229 (5)	-0.278 (2)	0.1718 (5)	4.1 (2)
C8	1.0775 (4)	-0.135 (1)	0.2093 (4)	3.6 (2)
C9	0.8207 (4)	0.817 (1)	0.4411 (4)	3.2 (2)
C10	0.7742 (4)	0.980 (1)	0.4850 (4)	3.1 (2)
C11	0.7236 (5)	1.187 (2)	0.4381 (5)	4.5 (2)
C12	0.6712 (5)	1.319 (2)	0.4812 (5)	4.9 (2)
C13	0.5970 (5)	1.174 (2)	0.4903 (5)	4.3 (2)

Table 2. Geometric parameters (Å, °)

S—C1	1.727 (8)	C3—C4	1.38 (1)
S—C2	1.812 (7)	C3—C8	1.39 (1)
O1—C9	1.243 (8)	C4—C5	1.37 (1)
O2—C9	1.239 (8)	C5—C6	1.39 (1)
O3—C10	1.198 (8)	C6—C7	1.36 (1)
O4—C13	1.23 (1)	C7—C8	1.38 (1)
O5—C13	1.29 (1)	C9—C10	1.53 (1)
N1—C1	1.318 (9)	C10—C11	1.49 (1)
N2—C1	1.308 (8)	C11—C12	1.50 (1)
C2—C3	1.52 (1)	C12—C13	1.51 (1)
C1—S—C2	103.1 (4)	C3—C8—C7	119.3 (8)
S—C1—N1	115.8 (5)	O1—C9—O2	125.6 (8)
S—C1—N2	123.7 (6)	O1—C9—C10	115.8 (6)
N1—C1—N2	120.5 (7)	O2—C9—C10	118.6 (6)
S—C2—C3	110.0 (5)	O3—C10—C9	119.9 (7)
C2—C3—C4	118.7 (7)	O3—C10—C11	122.8 (8)
C2—C3—C8	121.3 (7)	C9—C10—C11	117.2 (7)
C4—C3—C8	119.9 (8)	C10—C11—C12	114.1 (7)
C3—C4—C5	120.8 (8)	C11—C12—C13	113.8 (8)
C4—C5—C6	118.8 (8)	O4—C13—O5	124.5 (9)
C5—C6—C7	120.6 (9)	O4—C13—C12	121.6 (9)
C6—C7—C8	120.5 (8)	O5—C13—C12	113.9 (9)

Table 3. Contact distances (Å)

O(1)···N(1)	2.757 (9)	O(2)···N(2 ⁱⁱ)	2.844 (7)
O(1)···N(1')	2.785 (8)	O(4)···O(5 ⁱⁱⁱ)	2.653 (9)
O(2)···N(2)	2.889 (9)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $2 - x, 1 - y, 1 - z$;
(iii) $1 - x, 2 - y, 1 - z$.

Non-H atoms were refined anisotropically; H atoms were generated geometrically and allowed to ride on their parent C or N atoms (C—H = 0.95 Å, B = 5 Å²).

Data collection: CAD-4 diffractometer software (Enraf-Nonius, 1988). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1018). 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-(4-Chlorophenylazo)-1,3-indandione

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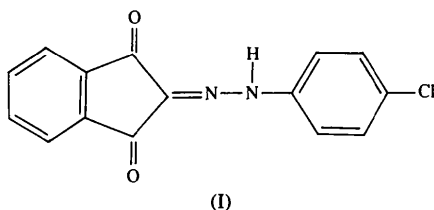
(Received 15 August 1994; accepted 25 October 1994)

Abstract

In the title compound, 2-(4-chlorophenylhydrazono)-1,3-indandione (C₁₅H₉ClN₂O₂), the indandione and phenylazo groups are connected by a C=N bond of 1.307 (3) Å. The molecule is planar and the bond lengths correspond to those expected for a phenylhydrazone. A strong intramolecular N—H···O hydrogen bond was found.

Comment

This crystal structure analysis is part of our program of structural investigation of azo compounds, and was undertaken to establish whether the hydrazone or azo tautomer is present. Experimental and theoretical studies of ground and excited states in molecules containing the azo-hydrazone tautomer system have shown that the hydrazone form is more stable than the azo form (Bigelow, 1976; Pendergrass, Paul & Curtin, 1972). Our work shows that this is true in the solid state for the title compound. In the azo form, with an O—H group, C(2)—C(3) would have to be a double bond, and C(3)—O(1) single, or C(2)—C(1) double and C(1)—O(2) single; this is not consistent with the observed bond lengths.



The bond lengths and angles agree with those in 2-phenylazo-1,3-indanedione (Ide, Kendi, Özbey & Ertan, 1994), which is also in the hydrazone form. The introduction of chlorine has no significant effect on the geometry of the molecule. The C(2)—N(2) and N(1)—N(2) bond lengths suggest considerable conjugation in this part of the molecule. The benzene ring plane is very slightly twisted from that of the hydrazone group [N(2)—N(1)—C(1')—C(2') = -178.2 (2)°], and the whole indanedione group is planar. In contrast, in 2-methyl-2-(4-chlorophenylazo)-1,3-indanedione (Özbey, Kendi, Hocaoglu, Uyar & Mak, 1993) and in 2-methyl-2-(4-nitrophenylazo)-1,3-indanedione (Özbey, Kendi, Hocaoglu, Uyar, Mak & Cascarano, 1994), the five-membered ring is in an envelope conformation.

There is an intramolecular hydrogen bond, N(1)—H...O(2), of 2.857 (2) Å.

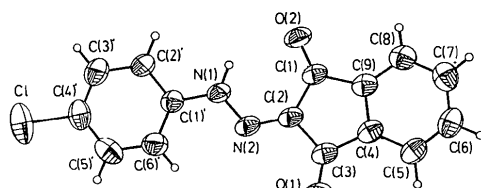


Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

Experimental

2-(4-Chlorophenylazo)-1,3-indandione was first synthesized and characterized by UV, IR, NMR and mass spectroscopy by

Hocaoglu, Uyar & Türker (1990). The compound was obtained by Japp-Kligemann reaction. *p*-Chloroaniline was diazotized and coupled with 2-acetyl-1,3-indandione. Recrystallization from ethanol yielded orange crystals, m.p. 517–519 K.

Crystal data

C₁₅H₉ClN₂O₂
M_r = 284.7
 Monoclinic
*P*2₁/*c*
a = 10.888 (2) Å
b = 9.329 (1) Å
c = 12.628 (1) Å
 β = 95.03 (1)°
V = 1277.7 (3) Å³
Z = 4
D_x = 1.480 Mg m⁻³

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 7.5–17.5°
 μ = 0.301 mm⁻¹
T = 298 K
 Needle
 0.80 × 0.32 × 0.26 mm
 Orange

Data collection

Siemens R3m/V diffractometer
 ω -2 θ scans
 Absorption correction: empirical
 3294 measured reflections
 2949 independent reflections
 2149 observed reflections
 [*F* > 4 σ (*F*)]

θ_{\max} = 27.5°
h = -14 → 14
k = 0 → 12
l = 0 → 16
 2 standard reflections monitored every 100 reflections
 intensity decay: insignificant

Refinement

Refinement on *F*
R = 0.0476
wR = 0.0567
S = 2.22
 2149 reflections
 217 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0002F^2]$
 $(\Delta/\sigma)_{\max} = 0.1$
 $\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from SHELXTL-Plus (Sheldrick, 1991)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl	0.9710 (1)	0.1631 (1)	0.3148 (1)	0.098 (1)
N(1)	1.3705 (2)	0.5807 (2)	0.4222 (1)	0.047 (1)
N(2)	1.3786 (2)	0.6507 (2)	0.5130 (1)	0.047 (1)
O(1)	1.4054 (2)	0.8331 (2)	0.6994 (1)	0.061 (1)
O(2)	1.5927 (1)	0.7278 (2)	0.3845 (1)	0.061 (1)
C(1')	1.2736 (2)	0.4830 (2)	0.3988 (2)	0.047 (1)
C(2')	1.2694 (2)	0.4077 (3)	0.3037 (2)	0.053 (1)
C(3')	1.1769 (2)	0.3098 (3)	0.2780 (2)	0.062 (1)
C(4')	1.0876 (2)	0.2875 (3)	0.3469 (2)	0.064 (1)
C(5')	1.0917 (2)	0.3610 (3)	0.4422 (3)	0.071 (1)
C(6')	1.1838 (2)	0.4587 (3)	0.4680 (2)	0.061 (1)
C(1)	1.5706 (2)	0.7806 (2)	0.4695 (2)	0.047 (1)
C(2)	1.4678 (2)	0.7435 (2)	0.5320 (2)	0.046 (1)
C(3)	1.4774 (2)	0.8315 (2)	0.6301 (2)	0.049 (1)
C(4)	1.5886 (2)	0.9210 (2)	0.6248 (2)	0.049 (1)
C(5)	1.6384 (2)	1.0210 (3)	0.6975 (2)	0.059 (1)
C(6)	1.7441 (3)	1.0923 (3)	0.6733 (2)	0.067 (1)
C(7)	1.7971 (2)	1.0663 (3)	0.5795 (2)	0.067 (1)
C(8)	1.7474 (2)	0.9659 (3)	0.5071 (2)	0.059 (1)
C(9)	1.6428 (2)	0.8934 (2)	0.5305 (2)	0.048 (1)

Table 2. Selected geometric parameters (Å, °)

Cl—C(4')	1.741 (3)	N(1)—N(2)	1.315 (2)
N(1)—C(1')	1.405 (3)	N(2)—C(2)	1.307 (3)
O(1)—C(3)	1.225 (3)	O(2)—C(1)	1.224 (3)
C(1')—C(2')	1.389 (3)	C(1')—C(6')	1.386 (3)
C(2')—C(3')	1.377 (3)	C(3')—C(4')	1.375 (4)
C(4')—C(5')	1.383 (4)	C(5')—C(6')	1.373 (4)
C(2)—C(3)	1.482 (3)	C(2)—C(1)	1.466 (3)
C(3)—C(4)	1.477 (3)	C(4)—C(5)	1.386 (3)
C(4)—C(9)	1.398 (3)	C(5)—C(6)	1.387 (4)
C(6)—C(7)	1.384 (4)	C(7)—C(8)	1.385 (4)
C(8)—C(9)	1.379 (3)	C(9)—C(1)	1.487 (3)
N(2)—N(1)—C(1')	119.8 (2)	N(1)—N(2)—C(2)	118.8 (2)
N(1)—C(1')—C(2')	118.5 (2)	N(1)—C(1')—C(6')	122.2 (2)
C(2')—C(1')—C(6')	119.3 (2)	C(1')—C(2')—C(3')	120.5 (2)
C(2')—C(3')—C(4')	119.6 (2)	Cl—C(4')—C(3')	119.7 (2)
Cl—C(4')—C(5')	120.0 (2)	C(3')—C(4')—C(5')	120.3 (2)
C(4')—C(5')—C(6')	120.2 (3)	C(1')—C(6')—C(5')	120.0 (2)
N(2)—C(2)—C(3)	121.2 (2)	N(2)—C(2)—C(1)	130.3 (2)
C(3)—C(2)—C(1)	108.5 (2)	O(1)—C(3)—C(2)	127.0 (2)
O(1)—C(3)—C(4)	127.1 (2)	C(2)—C(3)—C(4)	105.9 (2)
C(3)—C(4)—C(5)	128.7 (2)	C(3)—C(4)—C(9)	110.1 (2)
C(5)—C(4)—C(9)	121.2 (2)	C(4)—C(5)—C(6)	117.4 (2)
C(5)—C(6)—C(7)	121.4 (2)	C(6)—C(7)—C(8)	121.0 (2)
C(7)—C(8)—C(9)	118.2 (2)	C(4)—C(9)—C(8)	120.7 (2)
C(4)—C(9)—C(1)	109.1 (2)	C(8)—C(9)—C(1)	130.2 (2)
O(2)—C(1)—C(2)	126.5 (2)	O(2)—C(1)—C(9)	127.1 (2)
C(2)—C(1)—C(9)	106.4 (2)		

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Isomers of 5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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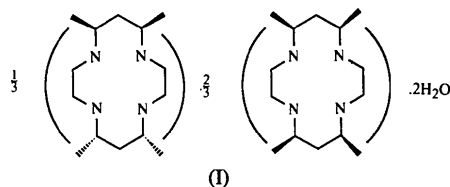
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Abstract

The structure of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane dihydrate, C₁₄H₃₂N₄·2H₂O, contains molecules of 5*SR*,7*RS*,12*RS*,14*SR*-tetramethyl-1,4,8,11-tetraazacyclotetradecane (which are centrosymmetric) and 5*SR*,7*RS*,12*SR*,14*RS*-tetramethyl-1,4,8,11-tetraazacyclotetradecane, with different macrocycle conformations and different configurations of the four chiral C atoms. The crystal structure is stabilized by hydrogen bonds.

Comment

Polyazamacrocyclic compounds have been studied extensively because they could be potential ligands in transition metal complexes (Lindoy, 1989). Previously, Kolinski & Korybut-Daszkiewicz (1975) described the preparation of the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The reduction of this ligand can result in five diastereoisomeric tetraamines *A* to *E*. Herein, we report the crystal and molecular structure of the diastereoisomers *A* and *B* of the reduction product, 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane, which crystallized as the dihydrate, (I).



The structure contains two independent molecules of the diastereoisomers *A* and *B*. The asymmetric unit contains half of molecule *A*, which has a crystallographic inversion center, molecule *B* in a general position and three disordered water molecules. In molecule *A* the four N atoms are exactly coplanar as a result of the sym-