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The Crystal and Molecular Structures of Three Isoquinoline Derivatives: 1-Chloro-3-hydroxyisoquinoline, 1-Phenyl-2-methyl-3-isoquinolone and 2-(2′,6′-Dichlorobenzyl)-1-isoquinolone

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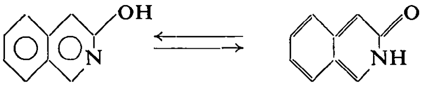
1-Chloro-3-hydroxyisoquinoline, C_9H_6ClNO, crystallizes in space group $P2_1/c$, with $a=9{\cdot}962$ (1), $b=5{\cdot}685$ (1), $c=14{\cdot}671$ (2) Å, $\beta=106{\cdot}360$ (9)°, $Z=4$. 1-Phenyl-2-methyl-3-isoquinolone, $C_{16}H_{13}NO$, crystallizes in space group $P2_1/m$, with $a=12{\cdot}580$ (2), $b=6{\cdot}869$ (2), $c=14{\cdot}247$ (2) Å, $\beta=97{\cdot}14$ (1)°, $Z=4$. There are two independent molecules on the crystallographic mirror plane. 2-(2′,6′-Dichlorobenzyl)-1-isoquinolone, $C_{16}H_{11}NOCl_2$, crystallizes in space group $P2_1/n$, with $a=9{\cdot}494$ (2), $b=11{\cdot}012$ (2), $c=14{\cdot}409$ (5) Å, $\beta=111{\cdot}02$ (1)°, $Z=4$. The cell constants and intensity data were collected with a Picker FACS-I diffractometer, Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å), and a graphite monochromator. The structures were solved by Patterson and direct methods and refined by the full-matrix least-squares technique with anisotropic temperature factors for C, N, O, Cl and isotropic terms for H. The structure of 1-chloro-3-hydroxyisoquinoline ($R=0{\cdot}045$) confirms the lactim tautomeric form of this compound in the solid state and provides an accurate set of bond lengths for the isoquinoline ring. Bond distances in the nitrogen-containing 6-ring of the 1-isoquinolone ($R=0{\cdot}038$) correspond more closely to the lengths in a 2-pyridone than do the 3-isoquinolone ($R=0{\cdot}084$) distances. The structure of homophthalimide, which is isostructural with 1-chloro-3-hydroxyisoquinoline, is reported in the Appendix. The compound, $C_9H_7NO_2$, crystallizes in space group $P2_1/c$ with cell constants $a=10{\cdot}040$ (6), $b=5{\cdot}814$ (3), $c=13{\cdot}256$ (5) Å, $\beta=104{\cdot}23°$ (5), $Z=4$. The structure refinement used anisotropic temperature factors for C, N and O. The H atoms were included at calculated positions, and the H parameters were not refined. The final R index was 0·114.

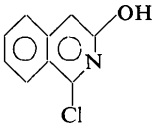
Introduction

Several ultraviolet spectroscopic investigations (Evans, Smith & Wahid, 1967; Jones, 1969) have shown that the 3-isoquinolinols (I, lactim form) are in facile equilibrium with the 3-isoquinolinones (II, lactam form). The equilibrium is readily shifted by a change in solvent polarity, with the lactam favored by polar solvents (*e.g.* water) and the lactim favored by nonpolar solvents (*e.g.* diethyl ether). However, the 1-chloro derivative (III) exists as the lactim in all solvent systems. The lactim form of 2-pyridones, for example, is favored by an electronegative substituent at C(6) of the pyridone ring (Katritzky, Rowe & Roy, 1967).



(I) (II)

Our X-ray crystallographic study of 1-chloro-3-hydroxyisoquinoline (III) was undertaken to confirm the lactim form in the solid state, and to provide bond lengths for the isoquinoline nucleus for which few structural data are available. In addition, 1-phenyl-2-methyl-3-isoquinolone (IV) and 2-(2′,6′-dichlorobenzyl)-1-isoquinolone (V) were studied as models for the 3-isoquinolinidene and 1-isoquinolinidene moieties.



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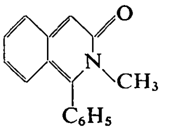

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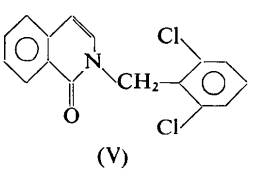

(V)

A comparison of the structural features of these isoquinolinoid nuclei with those in several pseudo-aromatic cyclopentadienylidenedihydroisoquinolines will be the subject of a future paper.

Experimental

Compound preparation

1-Chloro-3-hydroxyisoquinoline (III), prepared from homophthalimide by the method of Gabriel (1886), crystallized from ethanol at 0°C as colorless needles, m.p. 193–5° (lit 198°).

1-Phenyl-2-methyl-3-isoquinolone (IV) was prepared by mixing 6 g (0·02 mol) 1-phenyl-3-isoquinolinol (Jones, 1969, and references therein) with 40 ml methyl iodide and 3 ml of a saturated methanolic KOH solution. The mixture was refluxed for 24 h, then cooled and filtered to remove an inorganic residue. Evaporation of the CH_3I *in vacuo* left an oily yellow solid which proved to be a mixture of *N*-methyl and *O*-methyl products. Repeated recrystallization of the crude mixture from CCl_4 led to the isolation of the pure isoquinolone (IV). (IV) could also be separated by column chromatography (neutral alumina) using ether and then ethyl acetate as eluents; the isoquinolone was obtained in 45% yield from the dark yellow ethyl acetate fraction. Recrystallization from CCl_4, followed by recrystallization from acetone, gave light-yellow crystals, m.p. 136–140 °C. The structure of the product was confirmed by n.m.r., infrared and elemental analysis.

2-(2′,6′-Dichlorobenzyl)-1-isoquinolone (V) was prepared by treating 110 g (0·3 mol) of 1-(2′,6′-dichlorobenzyl)isoquinolinium bromide (Wheeler, 1973) with solutions of 113 g KOH (2·0 mol in 500 ml H_2O) and 210 g $K_3Fe(CN)_6$ (1·5 mol in 500 ml H_2O). Three recrystallizations from cyclohexane with Norite yielded 14·7 g (16%) of colorless material, m.p. 143–145°. The structure of the product was confirmed by n.m.r., infrared and elemental analysis.

X-ray measurements

The experimental techniques and data analysis employed here were described previously (Wheeler & Ammon, 1974). All the X-ray data were measured with a Picker FACS-I diffractometer, using Mo *Kα* radiation (0·71069 Å) and a graphite monochromator. Lenhert's (Lenhert & Henry, 1970) PDP-8I disc-oriented program system was used for diffractometer control. Crystal and intensity measurement data are presented in Table 1.

Structure determinations

The major calculations were carried out on the University of Maryland UNIVAC 1108 with the X-RAY system of crystallographic programs (1972).

1-*Chloro*-3-*hydroxyisoquinoline* (III): the chlorine position was deduced from a sharpened origin-removed Patterson map using Harker peaks. An electron-density map phased with the Cl revealed a chemically

Table 1. *Crystal data and intensity measurement information*

	1-Chloro-3-hydroxy-isoquinoline (II)	1-Phenyl-2-methyl-3-isoquinolone (III)	2-(2′,6′-Dichlorobenzyl)-1-isoquinolone (IV)
Molecular formula	C_9H_6ClNO	$C_{16}H_{13}NO$	$C_{16}H_{11}NOCl_2$
Crystallization solvent	Ethanol	Acetone at 0°C	Cyclohexane
Crystal size	Needle, 0·2 × 0·4 mm	Needle, 0·3 × 0·5 mm	Needle, 0·25 × 0·45 mm
Space group	$P2_1/c$	$P2_1/m$	$P2_1/n$
Unit-cell parameters	a = 9·962 (1) Å b = 5·685 (1) c = 14·671 (2) β = 106·36 (1)°	a = 12·580 (2) Å b = 6·869 (2) c = 14·247 (2) β = 97·14 (1)°	a = 9·494 (2) Å b = 11·012 (2) c = 14·409 (5) β = 111·01 (2)°
Average $\lvert 2\theta_o - 2\theta_c \rvert$	0·004°	0·003°	0·003°
Z	4	4	4
V	797 Å^3	1221 Å^3	1406 Å^3
ϱ (exp) [neutral buoyancy in aq. KI]	1·492 g cm^{-3}	1·282 g cm^{-3}	1·440 g cm^{-3}
ϱ (X-ray)	1·496 g cm^{-3}	1·279 g cm^{-3}	1·437 g cm^{-3}
Reciprocal-lattice vector parallel to diffractometer φ axis	[040]	[020]	[402]
2θ Scan, scan speed	2·0°, 1° min^{-1}	2·8°, 1° min^{-1}	1·5°, 1° min^{-1}
Time per background	20 s	20 s	40 s
Max 2θ, sin θ/λ	55°, 0·6497	55°, 0·6497	55°, 0·6497
Instability factor	none calculated	1·96 × 10^{-4}	8·09 × 10^{-5}
Total data measured including standards, unique data, data 3σ above background	2301, 1812, 1547	3349, 3054, 1619	2886, 2477, 1984

Table 2. *Fractional coordinates, temperature factors* (Å^2) *and e.s.d.'s for* 1-*chloro*-3-*hydroxyisoquinoline*

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·2951 (3)	0·3800 (6)	0·4801 (2)	0·052 (2)	0·060 (2)	0·041 (1)	−0·007 (2)	0·020 (1)	−0·005 (1)
C(3)	0·4407 (3)	0·2597 (6)	0·3942 (2)	0·052 (2)	0·059 (2)	0·042 (2)	−0·003 (2)	0·020 (1)	−0·003 (1)
C(4)	0·3939 (3)	0·4303 (6)	0·3272 (2)	0·058 (2)	0·062 (2)	0·045 (2)	−0·003 (2)	0·021 (1)	0·002 (2)
C(4*A*)	0·2909 (3)	0·5877 (6)	0·3376 (2)	0·054 (2)	0·057 (2)	0·045 (2)	−0·011 (2)	0·012 (1)	0·001 (1)
C(5)	0·2364 (4)	0·7700 (7)	0·2718 (2)	0·066 (2)	0·066 (2)	0·060 (2)	0·002 (2)	0·015 (2)	−0·011 (2)
C(6)	0·1387 (4)	0·9195 (7)	0·2857 (3)	0·069 (2)	0·065 (2)	0·074 (2)	0·002 (2)	0·008 (2)	0·015 (2)
C(7)	0·0876 (4)	0·8995 (7)	0·3662 (3)	0·060 (2)	0·064 (2)	0·084 (3)	0·009 (2)	0·016 (2)	−0·003 (2)
C(8)	0·1357 (4)	0·7270 (7)	0·4309 (2)	0·058 (2)	0·066 (2)	0·063 (2)	−0·004 (2)	0·020 (2)	0·003 (2)
C(8*A*)	0·2375 (3)	0·5664 (6)	0·4185 (2)	0·050 (2)	0·054 (2)	0·048 (2)	0·005 (1)	0·012 (1)	0·004 (1)
N	0·3909 (2)	0·2325 (4)	0·4713 (2)	0·052 (1)	0·057 (2)	0·039 (1)	0·000 (1)	0·018 (1)	0·000 (1)
O	0·5392 (3)	0·1093 (5)	0·3861 (2)	0·074 (2)	0·071 (2)	0·054 (1)	0·016 (1)	0·036 (1)	0·011 (1)
Cl	0·23449 (9)	0·3303 (2)	0·57917 (6)	0·0811 (6)	0·0828 (6)	0·0580 (5)	−0·0110 (5)	0·0424 (4)	−0·0049 (5)
H(3)	0·556 (4)	0·005 (7)	0·423 (2)	0·07 (1)					
H(4)	0·442 (3)	0·443 (5)	0·277 (2)	0·050 (8)					
H(5)	0·281 (4)	0·786 (7)	0·219 (3)	0·10 (1)					
H(6)	0·902 (4)	0·546 (7)	0·258 (3)	0·09 (1)					
H(7)	0·018 (3)	1·004 (6)	0·375 (2)	0·08 (1)					
H(8)	0·098 (3)	0·704 (5)	0·483 (2)	0·057 (9)					

reasonable fragment of seven new atoms. The remainder of the structure was found in a subsequent map, phased with these eight atoms.

1-*Phenyl*-2-*methyl*-3-*isoquinolone* (IV): an *E* map phased by direct methods (264 phases) showed a large number of peaks on the mirror planes, and little else in the rest of the asymmetric unit. This suggested that there were two independent molecules in the cell, both of which lay on a crystallographic mirror plane. Confirmation of this location was obtained from the Patterson function which revealed a huge slab-like peak at $y=0$. The structure solution was achieved by picking out the 12 largest *E*-map peaks, followed by several rounds of structure-factor–electron-density and difference-map calculations.

2-(2′-6′-*Dichlorobenzyl*)-1-*isoquinolone*(V): this com-

Table 3. *Fractional coordinates, temperature factors* (Å^2) *and e.s.d.'s for* 1-*phenyl*-2-*methyl*-3-*isoquinolone*

The population parameters of all atoms were 0·50, with the following exceptions: 1·0 for C(2*B*), C(3*B*), C(2*B*′), C(3*B*′), H(2*B*), H(3*B*), H(2*B*′), and H(3*B*′); 0·25 for H(9*A*), H(9*C*), H(9*A*′), and H(9*C*′). $r^*=0{\cdot}0039$ (1).

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·2645 (5)	0·25	0·3401 (4)	0·057 (4)	0·059 (5)	0·041 (4)	0·0	0·008 (3)	0·0
C(3)	0·2536 (6)	0·25	0·1648 (4)	0·124 (6)	0·049 (4)	0·041 (3)	0·0	0·017 (4)	0·0
C(4)	0·3693 (5)	0·25	0·1790 (4)	0·073 (5)	0·064 (5)	0·058 (4)	0·0	0·022 (4)	0·0
C(4*A*)	0·4289 (5)	0·25	0·2646 (4)	0·073 (5)	0·050 (4)	0·057 (4)	0·0	0·012 (3)	0·0
C(5)	0·5413 (6)	0·25	0·2733 (5)	0·062 (5)	0·102 (6)	0·085 (5)	0·0	0·028 (4)	0·0
C(6)	0·5971 (6)	0·25	0·3596 (6)	0·073 (5)	0·139 (8)	0·104 (6)	0·0	0·032 (5)	0·0
C(7)	0·5475 (6)	0·25	0·4441 (5)	0·066 (5)	0·148 (8)	0·094 (6)	0·0	0·000 (5)	0·0
C(8)	0·4405 (5)	0·25	0·4382 (4)	0·055 (4)	0·116 (6)	0·062 (4)	0·0	0·002 (3)	0·0
C(8*A*)	0·3765 (5)	0·25	0·3479 (4)	0·062 (5)	0·056 (5)	0·043 (4)	0·0	0·010 (3)	0·0
C(9)	0·0889 (5)	0·25	0·2443 (4)	0·058 (5)	0·072 (5)	0·067 (4)	0·0	−0·020 (3)	0·0
C(1*B*)	0·2065 (5)	0·25	0·4239 (4)	0·053 (4)	0·076 (5)	0·041 (4)	0·0	0·003 (3)	0·0
C(2*B*)	0·1796 (5)	0·0813 (8)	0·4645 (4)	0·181 (5)	0·091 (4)	0·111 (4)	0·058 (4)	0·092 (4)	0·033 (4)
C(3*B*)	0·1263 (5)	0·080 (1)	0·5439 (4)	0·183 (6)	0·119 (6)	0·116 (5)	0·045 (5)	0·095 (5)	0·060 (4)
C(4*B*)	0·1033 (6)	0·25	0·5850 (5)	0·084 (5)	0·146 (9)	0·053 (4)	0·0	0·025 (4)	0·0
N	0·2048 (4)	0·25	0·2522 (3)	0·060 (4)	0·047 (3)	0·041 (3)	0·0	−0·002 (3)	0·0
O	0·1931 (4)	0·25	0·0902 (3)	0·131 (4)	0·084 (4)	0·035 (3)	0·0	−0·013 (3)	0·0
H(4)	0·420 (3)	0·25	0·120 (3)	0·06 (1)					
H(5)	0·570 (4)	0·25	0·207 (3)	0·09 (2)					
H(6)	0·681 (5)	0·25	0·361 (4)	0·13 (2)					
H(7)	0·594	0·25	0·511	0·150					
H(8)	0·402 (5)	0·25	0·499 (4)	0·12 (2)					
H(9*A*)	0·058	0·25	0·172	0·150					
H(9*B*)	0·063	0·375	0·278	0·150					
H(9*C*)	0·065	0·25	0·312	0·150					
H(9*D*)	0·060	0·375	0·208	0·150					
H(2*B*)	0·191 (3)	−0·048 (7)	0·439 (3)	0·19 (2)					
H(3*B*)	0·105	−0·053	0·573	0·150					
H(4*B*)	0·068	0·25	0·648	0·150					
C(1′)	0·7548 (5)	0·25	0·9259 (4)	0·058 (4)	0·048 (4)	0·042 (3)	0·0	0·006 (3)	0·0
C(3′)	0·8222 (5)	0·25	0·7695 (4)	0·075 (4)	0·045 (4)	0·045 (3)	0·0	0·007 (3)	0·0
C(4′)	0·7124 (6)	0·25	0·7310 (4)	0·118 (6)	0·056 (5)	0·036 (3)	0·0	0·007 (3)	0·0
C(4*A*′)	0·6265 (5)	0·25	0·7834 (4)	0·058 (4)	0·052 (5)	0·056 (4)	0·0	0·003 (4)	0·0
C(5′)	0·5181 (6)	0·25	0·7411 (5)	0·084 (5)	0·083 (5)	0·067 (5)	0·0	−0·019 (4)	0·0
C(6′)	0·4382 (6)	0·25	0·7950 (6)	0·069 (5)	0·118 (7)	0·095 (6)	0·0	−0·010 (5)	0·0
C(7′)	0·4590 (6)	0·25	0·8969 (6)	0·065 (5)	0·134 (8)	0·097 (6)	0·0	0·002 (4)	0·0
C(8′)	0·5628 (5)	0·25	0·9379 (4)	0·056 (4)	0·098 (6)	0·078 (4)	0·0	0·012 (4)	0·0
C(8*A*′)	0·6496 (5)	0·25	0·8837 (4)	0·057 (4)	0·053 (4)	0·047 (4)	0·0	0·007 (3)	0·0
C(9′)	0·9489 (5)	0·25	0·9148 (4)	0·042 (4)	0·108 (6)	0·059 (4)	0·0	0·006 (3)	0·0
C(1*B*′)	0·7821 (4)	0·25	1·0302 (4)	0·044 (4)	0·074 (5)	0·038 (3)	0·0	0·013 (3)	0·0
C(2*B*′)	0·7921 (3)	0·0719 (7)	1·0786 (3)	0·080 (3)	0·064 (3)	0·050 (2)	−0·001 (3)	0·005 (2)	0·006 (2)
C(3*B*′)	0·8146 (3)	0·0763 (7)	1·1762 (3)	0·088 (3)	0·084 (4)	0·059 (3)	−0·003 (3)	0·013 (2)	0·018 (3)
C(4*B*′)	0·8263 (5)	0·25	1·2242 (5)	0·063 (5)	0·107 (7)	0·047 (4)	0·0	0·011 (3)	0·0
N′	0·8379 (4)	0·25	0·8713 (3)	0·054 (3)	0·051 (3)	0·039 (3)	0·0	0·013 (2)	0·0
O′	0·9012 (4)	0·25	0·7270 (3)	0·088 (4)	0·088 (4)	0·051 (3)	0·0	0·034 (3)	0·0
H(4′)	0·704 (4)	0·25	0·671 (3)	0·09 (2)					
H(5′)	0·513 (3)	0·25	0·676 (3)	0·07 (1)					
H(6′)	0·355 (5)	0·25	0·771 (4)	0·14 (2)					
H(7′)	0·396	0·25	0·939	0·150					
H(8′)	0·579	0·25	1·012	0·150					
H(9*A*′)	0·950	0·25	0·989	0·150					
H(9*B*′)	0·987	0·375	0·893	0·150					
H(9*C*′)	0·999	0·25	0·861	0·150					
H(9*D*′)	0·963	0·375	0·957	0·150					
H(2*B*′)	0·769 (3)	−0·043 (5)	1·036 (2)	0·10 (1)					
H(3*B*′)	0·824 (3)	−0·046 (6)	1·207 (2)	0·12 (1)					
H(4*B*′)	0·862 (4)	0·25	1·298 (4)	0·12 (1)					

pound was solved by direct methods in a single computer run starting with the intensity data and ending in an E map (561 phases) which revealed all of the C, N, O and Cl atoms.

Refinement

The structures were refined by full-matrix least-squares with anisotropic temperature factors for C, N, O and Cl, and isotropic terms for H. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=1/\sigma(F_o)^2$. The data which had been observed at less than $3\sigma(I_o)$ were included in the calculations only in those instances where I_c was greater than $3\sigma(I_o)$. In the calculations for the two isoquinolones, F_c was corrected for isotropic secondary extinction using equation (22) given by Larson (1970). In the atomic parameter tables, the extinction parameter is Larson's r^* and the form of the anisotropic temperature factors is $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{23}klb^*c^*)]$. The structure-factor tables are available.†

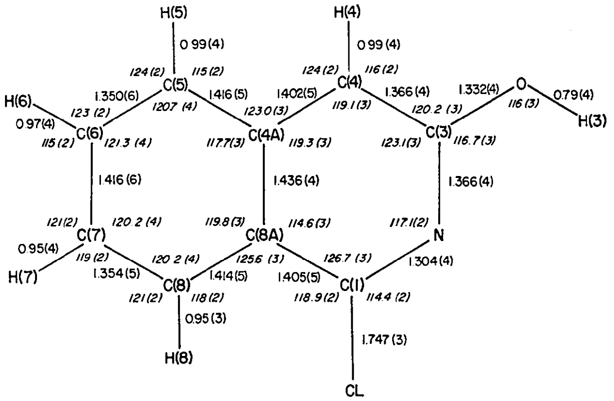

Fig. 1. Bond lengths (Å) and angles (°) for 1-chloro-3-hydroxyisoquinoline. Estimated standard deviations are in parentheses.

1-*Chloro*-3-*hydroxyisoquinoline* (III): the hydrogen atoms were located from a difference map. Cl dispersion corrections (Cromer & Liberman, 1970) were made. The final R $[\sum|F_o|-|F_c|/\sum F_o]$ and weighted R $[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2$; $w=1/\sigma^2(F_o)]$ factors were 0·045 and 0·032. Atomic parameters are given in Table 2.

1-*Phenyl*-2-*methyl*-3-*isoquinolone*(IV): the positions of the ring H atoms were calculated from the C atom locations with a C–H distance of 1·05 Å. The atoms were refined with isotropic temperature factors. Several H atoms showed substantial displacements from their original positions and developed large temperature factors; these atoms were placed in their initial locations and fixed with U's of 0·15 Å^2 in further refinement. The methyl H atoms, which appeared to have a

Table 4. *Fractional coordinates, temperature factors* (Å^2) *and e.s.d.'s for* 1-(2′,6′-*dichlorobenzyl*)-1-*isoquinolone*

$r^*=0·0134$ (2)

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·9542 (3)	0·1877 (2)	0·0057 (2)	0·035 (1)	0·061 (2)	0·036 (1)	0·007 (1)	0·011 (1)	−0·005 (1)
C(3)	0·9953 (3)	0·1576 (2)	0·1805 (2)	0·044 (2)	0·057 (2)	0·035 (1)	0·000 (1)	0·014 (1)	0·002 (1)
C(4)	1·1029 (3)	0·2421 (2)	0·2112 (2)	0·039 (1)	0·056 (2)	0·033 (1)	0·000 (1)	0·009 (1)	−0·003 (1)
C(4*A*)	1·1401 (3)	0·3120 (2)	0·1397 (2)	0·037 (1)	0·043 (1)	0·036 (1)	0·007 (1)	0·012 (1)	−0·001 (1)
C(5)	1·2464 (3)	0·4064 (2)	0·1668 (2)	0·053 (2)	0·051 (2)	0·042 (1)	−0·005 (1)	0·011 (1)	−0·003 (1)
C(6)	1·2772 (3)	0·4712 (3)	0·0950 (2)	0·068 (2)	0·058 (2)	0·058 (2)	−0·013 (2)	0·015 (2)	0·003 (1)
C(7)	1·2053 (4)	0·4444 (3)	−0·0046 (2)	0·079 (2)	0·072 (2)	0·053 (2)	−0·008 (2)	0·023 (2)	0·016 (2)
C(8)	1·1009 (3)	0·3517 (3)	−0·0334 (2)	0·055 (2)	0·071 (2)	0·038 (1)	−0·001 (2)	0·011 (1)	0·005 (1)
C(8*A*)	1·0666 (3)	0·2852 (2)	0·0378 (2)	0·037 (1)	0·048 (1)	0·035 (1)	0·006 (1)	0·012 (1)	0·002 (1)
C(9)	0·8024 (3)	0·0364 (2)	0·0540 (2)	0·045 (2)	0·049 (2)	0·056 (2)	−0·004 (1)	0·018 (1)	−0·012 (1)
C(1*B*)	0·6855 (3)	0·0567 (2)	0·1010 (2)	0·036 (1)	0·042 (1)	0·041 (1)	−0·006 (1)	0·010 (1)	−0·007 (1)
C(2*B*)	0·5784 (3)	0·1486 (2)	0·0688 (2)	0·043 (1)	0·043 (1)	0·041 (1)	−0·008 (1)	0·011 (1)	−0·004 (1)
C(3*B*)	0·4658 (3)	0·1673 (2)	0·1065 (2)	0·042 (2)	0·050 (2)	0·061 (2)	−0·003 (1)	0·018 (1)	−0·008 (1)
C(4*B*)	0·4597 (3)	0·0926 (3)	0·1813 (2)	0·050 (2)	0·076 (2)	0·059 (2)	−0·013 (2)	0·025 (1)	−0·014 (2)
C(5*B*)	0·5621 (3)	0·0021 (3)	0·2168 (2)	0·061 (2)	0·068 (2)	0·052 (2)	−0·020 (2)	0·022 (2)	0·003 (1)
C(6*B*)	0·6735 (3)	−0·0159 (2)	0·1772 (2)	0·044 (2)	0·047 (2)	0·055 (2)	−0·004 (1)	0·007 (1)	0·005 (1)
N	0·9192 (2)	0·1316 (2)	0·0811 (1)	0·034 (1)	0·052 (1)	0·036 (1)	−0·002 (1)	0·0112 (9)	−0·0052 (9)
O	0·8930 (2)	0·1558 (2)	−0·0814 (1)	0·053 (1)	0·091 (1)	0·0344 (9)	−0·012 (1)	0·0126 (9)	−0·014 (1)
Cl(2*B*)	0·58458 (9)	0·24675 (7)	−0·02442 (5)	0·0703 (5)	0·0682 (5)	0·0663 (5)	0·0063 (4)	0·0244 (4)	0·0211 (4)
Cl(6*B*)	0·8016 (1)	−0·13282 (8)	0·22629 (7)	0·0784 (6)	0·0769 (6)	0·1101 (7)	0·0182 (5)	0·0216 (5)	0·0402 (5)
H(3)	0·962 (2)	0·108 (2)	0·225 (1)	0·048 (6)					
H(4)	1·157 (2)	0·260 (2)	0·284 (1)	0·053 (6)					
H(5)	1·298 (2)	0·420 (2)	0·235 (1)	0·051 (6)					
H(6)	1·375	0·539	0·120	0·101					
H(7)	1·224 (3)	0·493 (2)	−0·058 (2)	0·073 (8)					
H(8)	1·048 (2)	0·330 (2)	−0·102 (2)	0·076 (7)					
H(9*A*)	0·756 (2)	0·040 (2)	−0·021 (1)	0·060 (7)					
H(9*B*)	0·851 (2)	−0·042 (2)	0·073 (2)	0·065 (7)					
H(3*B*)	0·391 (3)	0·236 (2)	0·077 (2)	0·084 (8)					
H(4*B*)	0·384 (2)	0·108 (2)	0·207 (2)	0·072 (7)					
H(5*B*)	0·559 (2)	−0·052 (2)	0·265 (1)	0·062 (7)					

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twofold disorder, were represented by six half-hydrogens (C–H = 1·07 Å) arranged to reflect the two 180° conformations of the methyl group that obey the mirror-plane symmetry. These atoms were not refined. The atomic parameters are given in Table 3. The final *R* and weighted *R* values were 0·084 and 0·068.

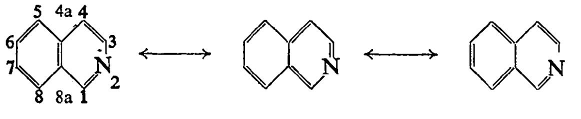
2-(2′,6′-*Dichlorobenzyl*)-1-*isoquinolone* (V): all hydrogen atoms were located in a difference map and refined, with the exception of H(6) which was fixed at its original difference map position. The atomic parameters are given in Table 4. The final *R* and weighted *R* values were both 0·038.

Scattering factors for C, N, O and Cl were generated from the analytical expressions of Cromer & Mann (1968); the factors for H were those of Stewart, Davidson & Simpson (1965).

Discussion

1-*Chloro*-3-*hydroxyisoquinoline*

The three principal valence bond structures of isoquinoline, (VI*a–c*), are similar to the naphthalene case, and predictions of $\frac{2}{3}$ double-bond character for C(1)–N, C(3)–C(4), C(5)–C(6) and C(7)–C(8) and $\frac{1}{3}$ double-bond character for the remaining bonds parallel naphthalene. The naphthalene distances, C(1)–C(2) = 1·361, C(2)–C(3) = 1·421, C(1)–C(8*A*) = 1·425, C(4*A*)–C(8*A*) = 1·410 Å, (numbering as in VI*a*; Cruickshank, 1957) show the same short-long pattern as III, Fig. 1. The two C–N lengths, C(1)–N = 1·304 Å and C(3)–N = 1·366 Å, have the expected relationship to the 1·340 Å C–N distance ($\frac{1}{2}$ double-bond character) in pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). The long and short C–C and C–N distances, which correspond to $\frac{1}{3}$ and $\frac{2}{3}$ double-bond character, respectively, are close to similar bonds in the 1,5-, 1,8- and 2,6-naphthyridines (Clearfield, Sims & Singh, 1972). The bond-length alternation together with the C(3)–O single-bond distance of 1·332 Å and the location of H on O confirms unequivocally that the compound has the lactim form in the solid state. The lactim C–O distances, for example 1·332 Å here, 1·330 Å in the 2-pyridone-6-chloro-2-hydroxypyridine complex (Almlöf, Kvick & Olovsson, 1971) and 1·321 Å in 6-chloro-2-hydroxypyridine (Kvick & Olovsson, 1968), are shorter than the 1·36–1·39 Å length typical of phenols. The differences may be associated with a small amount of C=O character (lactam form) in the hydroxypyridines and isoquinolines, or hybridization effects associated with the neighboring N atom.



(VI*a*) (VI*b*) (VI*c*)

The isoquinoline ring is almost planar (Table 5). The larger out-of-plane distances of C(1) and C(3) are probably caused by the Cl and O substituents.

Table 5. *Least-squares plane and deviations* (Å) *for* 1-*chloro*-3-*hydroxyisoquinoline*

$$5·9381\,x + 3·4848\,y + 4·8359\,z = 5·4134$$

	Deviation
C(1)	−0·015*
N	−0·003*
C(3)	0·015*
C(4)	0·007*
C(4*A*)	−0·005*
C(5)	−0·012*
C(6)	−0·004*
C(7)	0·012*
C(8)	0·010*
C(8*A*)	0·005*
Cl	−0·069
O	0·036

* Atoms used for plane definition.

Table 6. *Bond lengths* (Å), *angles* (°) *and e.s.d.'s for the two molecules of* 1-*phenyl*-2-*methyl*-3-*isoquinolone*

Hydrogen atoms are not included.

	Molecule	Molecule′	Average
C(1)—N	1·378 (7)	1·379 (8)	1·379
C(1)—C(1*B*)	1·474 (9)	1·483 (8)	1·479
C(1)—C(8*A*)	1·399 (9)	1·384 (8)	1·392
N——C(9)	1·449 (8)	1·455 (7)	1·452
C(3)—O	1·228 (7)	1·225 (8)	1·226
C(3)—C(4)	1·444 (10)	1·422 (9)	1·433
C(4)—C(4*A*)	1·350 (8)	1·387 (10)	1·368
C(4*A*)-C(8*A*)	1·428 (9)	1·423 (9)	1·426
C(5)—C(4*A*)	1·404 (10)	1·421 (9)	1·412
C(5)—C(6)	1·338 (11)	1·339 (11)	1·338
C(7)—C(8)	1·339 (10)	1·362 (9)	1·350
C(8)—C(8*A*)	1·430 (8)	1·413 (9)	1·421
C(1*B*)-C(2*B*)	1·357 (6)	1·402 (5)	1·380
C(2*B*)-C(3*B*)	1·385 (9)	1·384 (5)	1·385
C(3*B*)-C(4*B*)	1·356 (8)	1·373 (6)	1·364
C(1*B*)-C(1)—C(8*A*)	122·0 (5)	121·6 (5)	121·8
C(1*B*)-C(1)—N	117·9 (5)	117·9 (5)	117·9
C(8*A*)-C(1)—N	120·1 (5)	120·4 (5)	120·3
C(9)—N——C(1)	119·9 (5)	120·9 (5)	120·4
C(9)—N——C(3)	117·5 (5)	115·7 (5)	116·6
C(1)—N——C(3)	122·6 (5)	123·4 (5)	123·0
O——C(3)—N	117·3 (6)	118·6 (5)	117·9
O——C(3)—C(4)	128·8 (6)	128·2 (5)	128·5
N——C(3)—C(4)	113·9 (5)	113·2 (5)	113·5
C(4*A*)-C(4)—C(3)	124·3 (6)	125·2 (5)	124·8
C(5)—C(4*A*)-C(4)	121·3 (6)	122·9 (6)	122·1
C(4)—C(4*A*)-C(8*A*)	119·3 (6)	117·7 (6)	118·5
C(5)—C(4*A*)-C(8*A*)	119·4 (6)	119·4 (6)	119·4
C(6)—C(5)—C(4*A*)	119·3 (7)	120·5 (6)	119·9
C(7)—C(6)—C(5)	122·8 (7)	121·4 (7)	122·1
C(6)—C(7)—C(8)	119·4 (7)	118·4 (7)	118·9
C(7)—C(8)—C(8*A*)	120·4 (6)	122·0 (6)	121·2
C(8)—C(8*A*)-C(1)	121·4 (6)	121·7 (5)	121·5
C(4*A*)-C(8*A*)-C(8)	118·7 (6)	118·3 (5)	118·5
C(4*A*)-C(8*A*)-C(1)	119·9 (5)	120·0 (6)	120·0
C(1)—C(1*B*)-C(2*B*)	121·3 (3)	119·2 (3)	120·3
C(2*B*)-C(1*B*)-C(6*B*)*	117·4 (6)	121·5	119·4
C(1*B*)-C(2*B*)-C(3*B*)	121·8 (5)	118·0 (4)	119·6
C(2*B*)-C(3*B*)-C(4*B*)	119·8 (6)	121·0 (4)	120·4
C(3*B*)-C(4*B*)-C(5*B*)†	119·3 (6)	120·6 (5)	120·0

* C(6*B*) is the mirror image of C(2*B*).
† C(3*B*) is the mirror image of C(5*B*).

1-*Phenyl*-2-*methyl*-3-*isoquinolone*

There are two independent molecules of (IV) in the crystal. The isoquinolone atoms are centered on the crystallographic mirror plane in $P2_1/m$, and the phenyl nuclei are perpendicular to the mirror. The 2-methyl substituents show an apparent twofold disorder. Bond lengths and angles in the two molecules are listed in Table 6, and average values are presented in Fig. 2. The angles between the two unique four-atom phenyl fragments, C(1*A*) to C(4*A*), and the mirror are 88·9 and 89·5° (primed molecule).

The principal differences between the 3-hydroxy-isoquinoline and 3-isoquinolone structures are found in the *N*-containing 6-ring. The all-carbon 6-rings are quite similar because the amounts of C=C character in the isoquinoline are close to what would be expected for this ring in (IV). Bond lengths in the N 6-ring of (IV) reflect a substantial decrease in π-delocalization over that in the isoquinoline. The differences are largest in the C(1)–N–C(3)–C(4)–C(4*A*) region of (IV). The 1·44 Å C(3)–N distance indicates an almost complete absence of conjugation between these two atoms; the distance is 0·047 Å longer than the corresponding 1·400 Å length in 1-(2′,6′-dichlorophenyl)-2-pyridone (Wheeler & Ammon, 1974). The principal route for *N*-carbonyl conjugation may be *via* the long way around [from N to C(1) to C(8*A*), *etc*.], which could rationalize some of the bond-length differences, such as C(1)–C(8*A*), C(4)–C(4*A*) and C(3)–C(4), between the 3-isoquinolone and 2-pyridone.

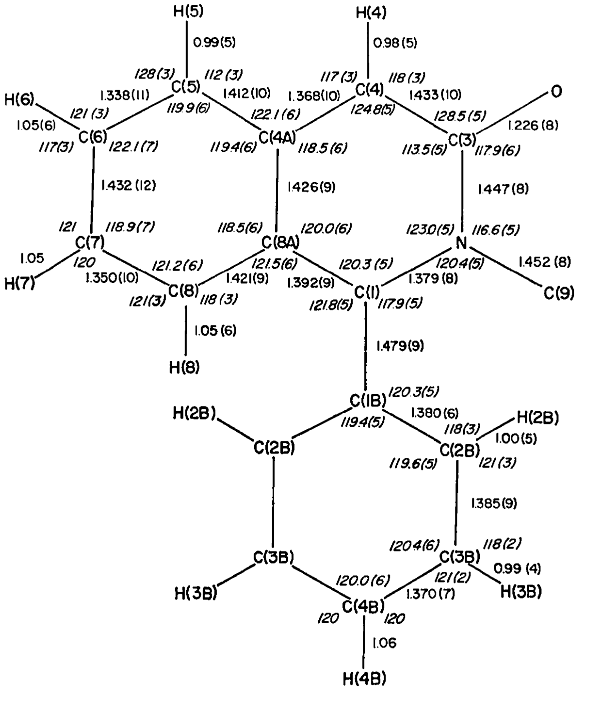


Fig. 2. Average bond lengths (Å) and angles (°) for 1-phenyl-2-methyl-3-isoquinolone. Estimated standard deviations are in parentheses.

2-(2′,6′-*Dichlorobenzyl*)-1-*isoquinolone*

The ten isoquinolone atoms deviate slightly from planarity (Table 7), the differences arising from the nitrogen-containing 6-ring, since the carbon 6-ring is rigorously planar. The angle between these two rings is 2·1°. The phenyl ring is planar and the isoquinolone–phenyl angle is 84·6°. This large an angle minimizes intramolecular interactions: corresponding angles of 85 and 87° were found in 1-(2′,6′-dichlorobenzyl)-2-pyridone and 1-(2′,6′-dichlorobenzyl)-2-ethoxypyridinium fluoroborate (Wheeler & Ammon, 1974).

Table 7. *Least-squares planes and deviations* (Å) *for* 2-(2′,6′-*dichlorobenzyl*)-1-*isoquinolone*

	Plane 1	Plane 2	Plane 3	Plane 4
C(1)	−0·033*	−0·032*	0·011	
N	0·050*	0·028*	0·110	1·217
C(3)	0·019*	0·001*	0·075	
C(4)	−0·032*	−0·023*	0·004	
C(4*A*)	−0·018*	0·016*	0·000*	
C(5)	0·001*	0·063	−0·003*	
C(6)	0·022*	0·108	0·002*	
C(7)	0·017*	0·099	0·001*	
C(8)	−0·009*	0·045	−0·004*	
C(8*A*)	−0·019*	0·011*	0·003*	
O	−0·112	−0·116		
C(9)	0·100	0·047		−0·057
C(1*B*)	1·230			−0·005*
C(2*B*)	2·557			0·007*
C(3*B*)	3·615			−0·003*
C(4*B*)	3·356			−0·002*
C(5*B*)	2·084			0·003*
C(6*B*)	1·033			0·000*
Cl(2*B*)	2·927			0·033
Cl(6*B*)	−0·570			0·016

Plane 1: $-7{\cdot}1086\,x+7{\cdot}2796\,y+3{\cdot}2251\,z=-5{\cdot}3649$
Plane 2: $-6{\cdot}9705\,x+7{\cdot}4558\,y+3{\cdot}1170\,z=-5{\cdot}2012$
Plane 3: $-7{\cdot}2094\,x+7{\cdot}1464\,y+3{\cdot}2904\,z=-5{\cdot}5299$
Plane 4: $3{\cdot}6353\,x+6{\cdot}8704\,y+7{\cdot}1844\,z=3{\cdot}6118$

The plane 1 to plane 2 angle is 2·1°.

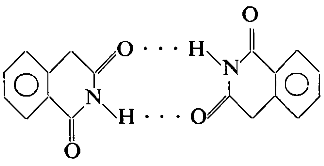
* Atoms used for plane definition.

With the exception of the C(4*A*)–C(8*A*) bond, which is common to both isoquinolone 6-rings, the bond distances in the nitrogen 6-ring (Fig. 3) closely parallel those in 1-(2′,6′-dichlorobenzyl)-2-pyridone (Wheeler & Ammon, 1974), whereas bond distances between the 3-isoquinolone 6-ring (IV) and the 2-pyridone differ by larger amounts. The greater similarity between the 6-ring structures of the 2-pyridone and the 1-isoquinolone (V), than between the 6-ring structures of the 2-pyridone and the 3-isoquinolone (IV), reflects the position of the benzo substituent relative to the 2-pyridone nucleus. The transformation of a 2-pyridone to a 1-isoquinolone involves addition of a –CH=CH–CH=CH– fragment across the C(3)–C(4) double bond of the pyridone, whereas transformation to a 3-isoquinolone requires addition to the C(4)–C(5) single bond of the pyridone. It is well-known that benzo annelation of a double bond results in a smaller structural change than annelation of a single bond, and the structural similarities between the pyridone and 1-isoquinolone are in accord with this experience.

Bond lengths calculated for 1-isoquinolone (Bodor, Dewar & Harget, 1970) are in good agreement with the experimental values for (V), with the exception of C(4)–C(4*A*) (calc. 1·462 Å) and the N–C=O region (calc. N–C = 1·376 Å, C=O = 1·265 Å). The calculated values appear to overestimate the $^{+}$N=C–O^{-} form of the amide.

Molecular packing

1-*Chloro*-3-*hydroxyisoquinoline*: a packing diagram showing molecules at x,y,z, $1-x,1-y,1-z$ and $1-x,-y,1-z$ is given in Fig. 4. The principal intermolecular interaction is the formation of a H-bonded dimer with the O–H···N moiety across a center of symmetry ($\frac{1}{2},0,\frac{1}{2}$ in Fig. 4). The H···N distance is considerably shorter than the 2·7 Å sum of the N and H van der Waals radii. The N···O distance is 2·83 Å and the O–H···N angle is 171°. The center at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ places the *N*-containing 6-rings in two molecules at a distance of 3·43 Å, which corresponds to the 3·4 Å van der Waals thickness of an aromatic ring. This 3·43 Å approach is between the two atoms, C(1) and C(3), which have the largest deviations from the least-squares plane of the isoquinoline ring (Table 5). The packing arrangement found in (III) is virtually identical to that observed in homophthalimide (VII) (see Appendix).



(VII)

1-*Phenyl*-2-*methyl*-3-*isoquinolone*: a packing diagram is given in Fig. 5. There are no particularly close approaches in the mirror plane, the molecular arrangement being governed solely by H···H interactions. The phenyl nuclei pack nicely into the void spaces between the isoquinolone rings. The phenyl rings at $y=\frac{3}{4}$ also fit into holes in the $y=\frac{1}{4}$ level. Portions of the isoquinolone rings at $y=\frac{1}{4}$ and $\frac{3}{4}$ overlap; the spacing

Table 8. *Fractional coordinates, temperature factors*(Å^2) *and e.s.d.'s for homophthalimide*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·271 (1)	0·389 (2)	0·4999 (7)	0·039 (5)	0·034 (5)	0·032 (5)	0·005 (4)	0·013 (4)	−0·004 (4)
C(3)	0·433 (1)	0·263 (2)	0·3937 (7)	0·040 (5)	0·051 (6)	0·025 (4)	0·001 (5)	0·014 (4)	0·004 (5)
C(4)	0·377 (1)	0·442 (2)	0·3134 (7)	0·051 (6)	0·049 (7)	0·028 (5)	0·013 (5)	0·020 (4)	0·014 (5)
C(4*A*)	0·2727 (9)	0·604 (2)	0·3366 (7)	0·035 (5)	0·035 (5)	0·028 (4)	0·002 (4)	0·006 (4)	0·001 (4)
C(5)	0·226 (1)	0·783 (2)	0·2697 (8)	0·049 (6)	0·040 (6)	0·037 (5)	0·000 (5)	0·007 (4)	0·009 (5)
C(6)	0·127 (1)	0·934 (2)	0·2890 (9)	0·061 (7)	0·037 (6)	0·049 (6)	0·002 (6)	−0·004 (5)	0·008 (5)
C(7)	0·075 (1)	0·902 (2)	0·3786 (9)	0·050 (6)	0·053 (7)	0·057 (7)	0·011 (6)	0·011 (5)	−0·011 (6)
C(8)	0·123 (1)	0·721 (2)	0·4464 (8)	0·045 (6)	0·047 (7)	0·036 (5)	0·010 (5)	0·011 (4)	−0·001 (5)
C(8*A*)	0·2208 (9)	0·575 (2)	0·4253 (7)	0·036 (5)	0·036 (5)	0·026 (4)	0·005 (4)	0·008 (4)	0·000 (4)
N	0·3762 (8)	0·249 (1)	0·4800 (6)	0·042 (4)	0·037 (5)	0·025 (4)	0·011 (4)	0·016 (3)	0·007 (4)
O(1)	0·2316 (8)	0·348 (1)	0·5773 (5)	0·061 (5)	0·057 (5)	0·033 (4)	0·019 (4)	0·031 (3)	0·008 (4)
O(3)	0·5231 (8)	0·132 (1)	0·3861 (5)	0·054 (4)	0·061 (5)	0·039 (4)	0·027 (4)	0·031 (3)	0·016 (4)

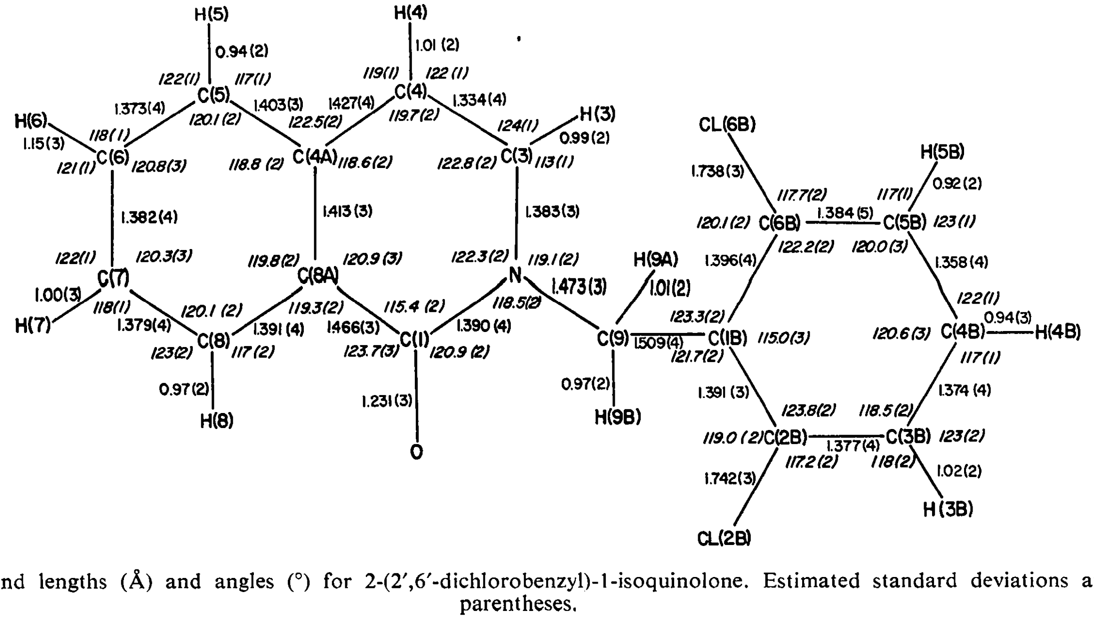


Fig. 3. Bond lengths (Å) and angles (°) for 2-(2′,6′-dichlorobenzyl)-1-isoquinolone. Estimated standard deviations are in parentheses.

between mirror planes of 3·43 Å (0·5b) corresponds to the thickness of an aromatic ring.

An interesting aspect is the difference in the phenyl thermal ellipsoids between the two molecules. The C(2B) and C(3B) ellipsoids are considerably larger than either the C(1B) or C(4B) ellipsoids (in the same ring) or the C(1B') to C(4B') ellipsoids. The principal axes of the C(2B) and C(3B) ellipsoids are perpendicular to the phenyl plane and suggest that the phenyl is either rocking about the C(1)–C(1B) bond or that the ring is disordered in a way which gives the appearance of a rocking motion. The more normal ellipsoids for the primed phenyl moiety may be due to the restricting methyl···phenyl interaction [C(9)···C(4B')] shown in Fig. 5. The other phenyl is relatively unfettered and thus has a better opportunity for rocking or disorder.

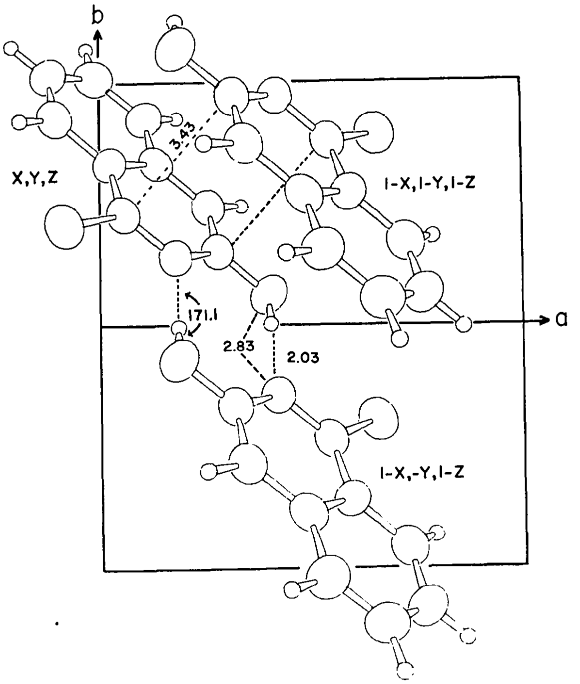


Fig. 4. An *ORTEP*-II (Johnson, 1971) packing diagram for 1-chloro-3-hydroxyisoquinoline normal to the *ab* plane.

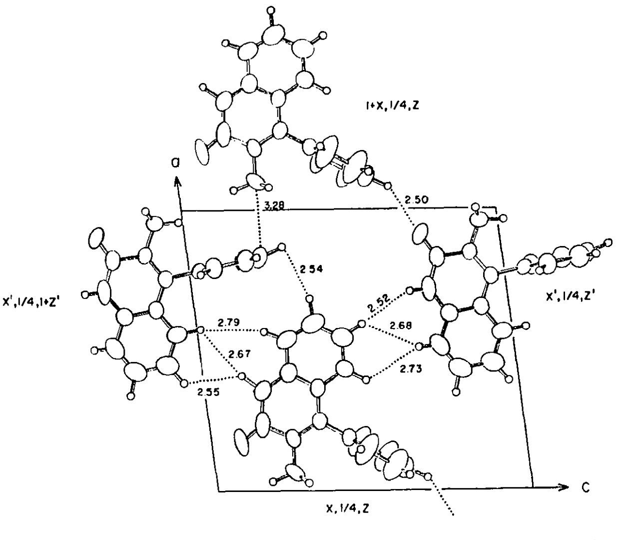


Fig. 5. An *ORTEP*-II (Johnson, 1971) packing diagram for 1-phenyl-2-methyl-3-isoquinolone normal to the crystallographic mirror plane at $y=\frac{1}{4}$. Two of the equivalent position indicators have been primed to differentiate the primed from the unprimed molecules.

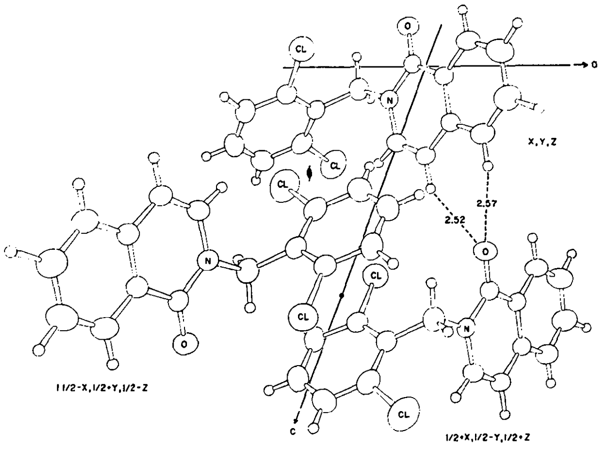


Fig. 6. An *ORTEP*-II (Johnson, 1971) packing diagram for 2-(2′,6′-dichlorobenzyl)-1-isoquinolone normal to the *ac* plane.

2-(2′,6′-Dichlorobenzyl)-1-isoquinolone: the packing is illustrated in Fig. 6. The only distances less than the normal van der Waals separations are the 2·57 Å H(5)···O and 2·52 Å H(4)···O.

The 2,6-dichlorobenzyl substituent was used in (V), and in the 2-pyridone and 2-ethoxypyridinium fluoroborate (Wheeler & Ammon, 1974), to increase the compounds' melting points and crystallinities. The origin of these effects, in terms of crystal packing, is unclear since the dichlorobenzyl moiety does not appear to have any close intermolecular contacts in any of the systems studied. In all cases, the shortest dichlorobenzyl contacts were larger than the corresponding van der Waals distances.

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APPENDIX

Homophthalimide crystallized from ethanol in the monoclinic space group $P2_1/c$. The least-squares cell parameters determined from 16 manually centered 2θ measurements are $a=10{\cdot}040(6)$, $b=5{\cdot}814(3)$, $c=13{\cdot}256\,(5)$ Å, $\beta=104{\cdot}23\,(5)^\circ$; $Z=4$. Data were collected as described in the experimental section: 0·5° min^{-1} θ–2θ scan, 40 s backgrounds, peak width $=2{\cdot}2^\circ$, maximum $2\theta=55^\circ$. Three standards were measured at 80 reflection intervals. 1615 data were measured: 1458 unique data; 981 data were 3σ above background.

The fact that the homophthalimide and 1-chloro-3-hydroxyisoquinoline unit-cell parameters and structures are quite similar, suggested that the two crystal structures could be isomorphous. This proved to be true, since homophthalimide was solved by using the fractional coordinates of (III) as a trial structure for the imide. The structure refinement used anisotropic temperature factors for C, N and O; the H atom positions were calculated, and these atoms were not refined. The final R index was 0·114.

The C, N and O atomic parameters are listed in Table 8 and bond lengths and angles are given Fig. 7. The structure factor table is available.*

The intermolecular hydrogen bonding is very close to the structure of 3. The 3-hydroxyisoquinoline N···H–O structure has been replaced by a N–H···O structure in homophthalimide. The H···O distance, based on an N–H length of 1·01 Å, is 1·86 Å.

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* See footnote on page 1149.

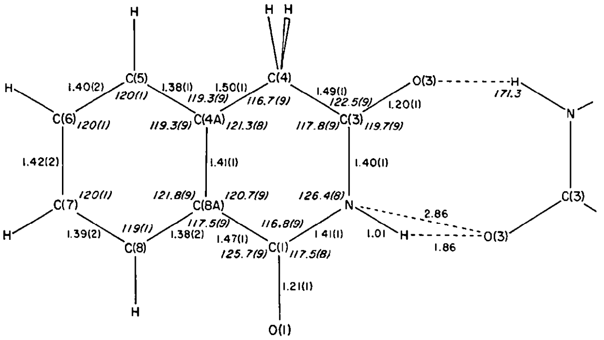

Fig. 7. Bond lengths (Å) and angles (°) for homophthalimide. Estimated standard deviations are in parentheses. A few intermolecular contacts have been included in the diagram.

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