

Datensammlung

Kuma KM-4 Diffraktometer $R_{\text{int}} = 0,023$
 ω - 2θ Abtastung $\theta_{\text{max}} = 70,54^\circ$
 Absorptionskorrektur: $h = -13 \rightarrow 13$
 ψ scan (North *et al.*, $k = -18 \rightarrow 19$
 1968) $l = 0 \rightarrow 20$
 $T_{\text{min}} = 0,384$, $T_{\text{max}} = 0,664$ 2 Kontrollreflexe
 10349 gemessene Reflexe alle 100 Reflexe
 9965 unabhängige Reflexe Intensitätsschwankung:
 7912 Reflexe mit 2,0%
 $I > 2\sigma(I)$

Verfeinerung

Verfeinerung auf F^2 $(\Delta/\sigma)_{\text{max}} = -0,001$
 $R[F^2 > 2\sigma(F^2)] = 0,045$ $\Delta\rho_{\text{max}} = 0,491 \text{ e } \text{Å}^{-3}$
 $wR(F^2) = 0,147$ $\Delta\rho_{\text{min}} = -0,375 \text{ e } \text{Å}^{-3}$
 $S = 1,173$ Extinktionskorrektur:
 9965 Reflexe $SHELXL93$ (Sheldrick,
 798 Parameter 1993)
 H-Atome: teils frei verfeinert, teils 'constrained' Extinktionskoeffizient:
 Berechnete Gewichtungen 0,0014 (2)
 $w = 1/[\sigma^2(F_o^2) + (0,0907P)^2 + 0,4225P]$ Atomformfaktoren aus
 wobei $P = (F_o^2 + 2F_c^2)/3$ *International Tables for Crystallography* (Vol. C)

Tabelle 2. Wasserstoffbrückengeometrie (Å, °) für (3)

D—H...A	D—H	H...A	D...A	D—H...A
O10A—H10A...N3B	0,72 (3)	2,50 (3)	3,134 (2)	147 (3)
O10A—H10A...O12B	0,72 (3)	2,40 (3)	3,029 (3)	147 (3)
O10B—H10B...N3A	0,72 (3)	2,32 (3)	2,988 (2)	155 (3)
O10B—H10B...O12A	0,72 (3)	2,58 (3)	3,171 (3)	140 (3)
O10C—H10C...N3D	0,82 (3)	2,21 (3)	2,962 (2)	152 (3)
O10C—H10C...O12D	0,82 (3)	2,48 (3)	3,152 (3)	139 (3)
O10D—H10D...N3C	0,76 (3)	2,39 (3)	3,092 (2)	153 (3)
O10D—H10D...O12C	0,76 (3)	2,53 (3)	3,164 (3)	141 (3)
C6B—H6C...O10A'	1,02 (2)	2,45 (2)	3,423 (3)	160 (2)
C8A—H8A1...O10C'	0,98 (2)	2,34 (2)	3,273 (3)	158 (2)
C8B—H8B2...N3D	0,91 (2)	2,46 (2)	3,292 (3)	151 (2)
C8C—H8C1...N3A''	0,97 (3)	2,47 (3)	3,332 (3)	148 (2)
C8D—H8D2...O10B'''	0,88 (3)	2,47 (3)	3,262 (3)	150 (2)

Symmetriebezeichnungen: (i) $2 - x, 2 - y, 1 - z$; (ii) $1 + x, y, z$; (iii) $2 - x, 1 - y, 1 - z$.

Die übrigen H-Atome in (3) wurden isotrop verfeinert. Bei der Bestimmung der Kristall-Polarität von (1) wurden 722 Friedel-Reflexpaare ausgewertet. Für Verbindung (1) wurde der Ursprung nach der Methode von Flack & Schwarzenbach (1988) festgelegt.

Beide Verbindungen, Datensammlung: *KM-4 Software* (Kuma Diffraction, 1991); Zellverfeinerung: *KM-4 Software*; Datenreduktion: *KM-4 Software*; Lösung der Strukturen: *SHELXS86* (Sheldrick, 1985); Verfeinerung der Strukturen: *SHELXL93* (Sheldrick, 1993). Molekülgrafik: *ORTEPII* (Johnson, 1976) und *PLUTO* (Motherwell & Clegg, 1978) für (1); *ORTEPII* für (3). Beide Verbindungen, Programm für die Herstellung von Veröffentlichungsmaterialien: *SHELXL93*.

Ergänzende Daten für diese Veröffentlichung können vom elektronischen Archiv des IUCr (Referenz: JZ1330) bezogen werden. Zugangsmöglichkeiten für diese Daten werden auf der dritten Umschlagseite beschrieben.

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Isoquinoline

KARL HENSEN,^a RALF MAYR-STEIN^a AND MICHAEL BOLTE^b

^aInstitut für Physikalische und Theoretische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany, and ^bInstitut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany. E-mail: bolte@chemie.uni-frankfurt.de

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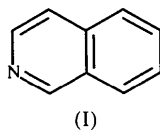
Abstract

Isoquinoline, C₉H₇N, is a ligand which is used as a complexing agent for different metals. In order to compare geometric features of free isoquinoline and isoquinoline as a complexing ligand, we determined its crystal structure. Regrettably, the molecule is located on a centre of inversion and is therefore disordered; it is also isostructural with naphthalene. By refinement experiments and packing considerations, we were able to discard the possibility of fourfold disorder, which has been found for several β -substituted naphthalene compounds, and performed the structure determination employing a model of twofold disorder.

Comment

Isoquinoline is a well known ligand that has been used in studies of the formation of various adducts of Group IVA halides (Miller & Onyszchuk, 1967). As

part of our ongoing investigations on the Si—N bond in silicon coordination compounds, we have crystallized the title compound, (I), in order to evaluate any possible structural differences between the coordinated and the uncoordinated forms of this ligand. Isoquinoline, (I), is isostructural with naphthalene, whose structure has been determined from single crystals on numerous occasions (Abrahams *et al.*, 1949; Ahmed & Cruickshank, 1952; Cruickshank, 1957; Ponomarev *et al.*, 1976; Brock & Dunitz, 1982) and by X-ray powder diffraction (Alt & Kalus, 1982). Furthermore, the structure of perdeuterio-naphthalene was determined by neutron diffraction at both ambient temperature (Pawley & Yeats, 1969) and 12 K (Natkaniec *et al.*, 1983). Whereas all naphthalene structures have previously been refined in space group $P2_1/a$, we have chosen space group $P2_1/c$ in the standard setting. After transforming our cell parameters to $P2_1/a$ using the matrix (001/010/101), the values obtained show that the structures of naphthalene and isoquinoline are in fact isostructural.



Since the molecule is located on a centre of inversion, it must be disordered. In principle, there are two possibilities of disorder: the N atom can be located at positions 2 and 2' of the aromatic system with an occupancy of 0.5 each, or it can be located on four positions, namely 2, 2', 3 and 3'. In the latter case, the sum of the four site-occupation factors for the N atoms is constrained to 1, but their ratio has to be determined. Our refinement experiments revealed that the N atom shows only a twofold disorder, occupying positions 2 and 2' with an occupancy of 0.5 each (see *Experimental*). A close inspection of the crystal packing reveals that positions 2 and 3 of the aromatic moiety have a different environment: the H atom at C3 points towards the centre of a neighbouring aromatic ring. This arrangement, which brings a $\delta(+)$ H atom of one aromatic group into close contact with the $\delta(-)$ π -electron cloud of another aromatic ring, has been found in many crystal structures (Burley & Petsko, 1986) and was calculated to be favourable by *ab initio* methods (Pawliszym *et al.*, 1984). The H atom at C2, on the other hand, appears to be rather close to the N atom [$\text{H2} \cdots \text{N2}^i$ 2.92 (3) Å and $\text{C2} - \text{H2} \cdots \text{N2}^i$ 128.6 (19)°; symmetry code: (i) $-x + 2, -y + 1, -z + 2$]. In addition to the refinement experiments, this consideration makes it plausible that the N atom shows only a twofold disorder. Disorder has also been found for β -substituted naphthalene compounds: 2-fluoronaphthalene (Chanh & Haget-Bouillaud, 1972; Meresse *et al.*, 1979), 2-chloronaphthalene (Chanh *et al.*, 1970; Meresse *et al.*, 1980), 2-bromonaphthalene (Chanh *et al.*, 1973), 2-methylnaphthalene (Meresse *et al.*, 1983), β -naphthol (Watson & Hargreaves, 1958; Coppens & Hairfield, 1965) and 2-naphthalenethiol (Chanh *et al.*, 1984) undergo a phase transition from an ordered low-temperature form to a disordered high-temperature form, and this high-temperature form is very similar in structure to unsubstituted naphthalene, but it is not exactly isostructural with the latter and the substituent in the β position is fourfold disordered. This fourfold disorder, in contrast to the twofold disorder of the title compound, can be explained by the crystal packing; in the β -substituted naphthalene compounds, the substituents at positions 2 and 3 are in a similar environment, which is not the case for isoquinoline. In conclusion, it can be stated that the different kinds of disorder in isoquinoline and β -substituted naphthalenes are in agreement with the different crystal packing.

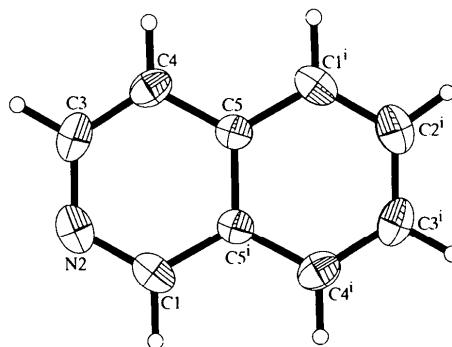


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level. Atoms N2 and C2 share the same site (occupancy 0.5 each) and they were refined with the same anisotropic displacement parameters. Only one of the two atoms is shown in each symmetry equivalent position [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

Experimental

Commercial isoquinoline was purified by distillation from calcium hydride and stored under vacuum. The substance crystallized at 293 K within a few hours. Elemental analysis (C₉H₇N): calculated C 83.7, H 5.5, N 10.8%; found: C 83.3, H 5.8, 10.7%.

Crystal data

C₉H₇N
M_r = 129.16
 Monoclinic
 $P2_1/c$
 $a = 7.839$ (2) Å
 $b = 5.990$ (1) Å
 $c = 8.244$ (2) Å
 $\beta = 116.88$ (1)°
 $V = 345.28$ (13) Å³
 $Z = 2$
 $D_x = 1.242$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 8192 reflections
 $\theta = 1-25^\circ$
 $\mu = 0.074$ mm⁻¹
 $T = 173$ (2) K
 Block
 0.60 × 0.50 × 0.40 mm
 Colourless

Data collection

Siemens CCD three-circle diffractometer	916 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.034$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 30.51^\circ$
$T_{\text{min}} = 0.957, T_{\text{max}} = 0.971$	$h = -11 \rightarrow 11$
11 083 measured reflections	$k = -8 \rightarrow 8$
1049 independent reflections	$l = -11 \rightarrow 11$
	146 standard reflections
	frequency: 1200 min
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0470$	$\Delta\rho_{\text{max}} = 0.305 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1331$	$\Delta\rho_{\text{min}} = -0.191 \text{ e } \text{\AA}^{-3}$
$S = 1.092$	Extinction correction: none
1049 reflections	Scattering factors from
62 parameters	<i>International Tables for</i>
H atoms refined isotropically	<i>Crystallography</i> (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 0.0434P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C1	0.73107 (14)	0.65467 (18)	0.62301 (14)	0.0388 (3)
C2†	0.83598 (13)	0.5109 (2)	0.76036 (13)	0.0456 (3)
N2†	0.83598 (13)	0.5109 (2)	0.76036 (13)	0.0456 (3)
C3	0.75575 (15)	0.30850 (19)	0.77331 (13)	0.0424 (3)
C4	0.57319 (15)	0.24817 (16)	0.65165 (12)	0.0363 (3)
C5	0.45989 (11)	0.39596 (14)	0.50750 (11)	0.0284 (2)

† Site occupancy = 0.50.

Table 2. Selected geometric parameters ($\text{\AA}, ^\circ$)

C1—C2	1.3631 (16)	C3—C4	1.3736 (15)
C1—C5'	1.4261 (13)	C4—C5	1.4249 (13)
C2—C3	1.3919 (17)	C5—C5'	1.4265 (16)
C2—C1—C5'	121.71 (9)	C4—C5—C1'	122.88 (9)
C1—C2—C3	119.35 (9)	C4—C5—C5'	118.82 (10)
C4—C3—C2	122.06 (9)	C1'—C5—C5'	118.29 (10)
C3—C4—C5	119.76 (9)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.Table 3. C—H...N intermolecular contacts ($\text{\AA}, ^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...N2'	0.98 (3)	2.92 (3)	3.613 (2)	128.6 (19)
C4—H4...N2''	0.985 (16)	3.161 (16)	3.8650 (16)	129.7 (11)
C1—H1...N2'''	1.024 (16)	2.922 (15)	3.7477 (16)	138.2 (11)

Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

For refinement of position 2 of the isoquinoline system, a C and an N atom (both with site occupancy 0.5) were placed on the same site with the same displacement parameters, a procedure which did not introduce any additional parameters to the refinement. In order to prove that the N atom is disordered over just two positions, we performed the following refinement: for positions 2 and 3 of the isoquinoline ring, a C and an N atom were introduced, sharing the same site and the same displacement parameters, but the occupation factors

of these different atoms were allowed to refine employing the constraints that the sum of the occupation factors of two atoms sharing the same site must sum to 1.0 and that the sum of the two occupation factors of the C atoms must sum to 1.5, implying that the occupation factors of the two N atoms must sum to 0.5. The refinement resulted in the following site-occupation factors: C2 0.578 (4), N2 0.422 (4), C3 0.922 (4) and N3 0.078 (4). This result should be sufficient proof of the twofold disorder. All H atoms were located by difference Fourier synthesis and refined freely.

Data collection: SMART (Siemens, 1995). Cell refinement: SMART. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1296). Services for accessing these data are described at the back of the journal.

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