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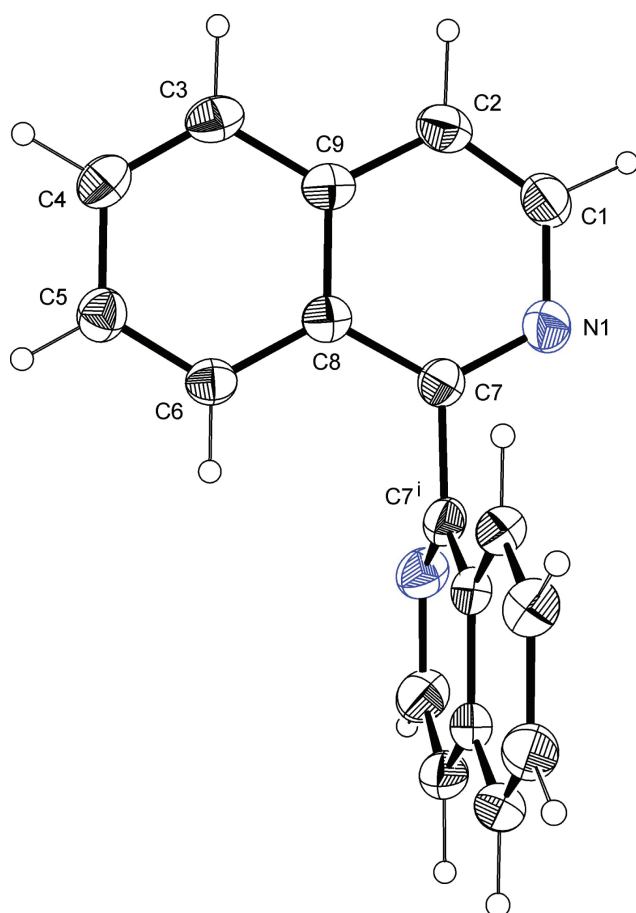
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**Table 1:** Data collection and handling.

| | |
|--|---|
| Crystal: | Yellow prism |
| Size: | 0.64 × 0.58 × 0.32 mm |
| Wavelength: | Mo $K\alpha$ radiation (0.71073 Å) |
| μ : | 0.8 cm ⁻¹ |
| Diffractometer, scan mode: | STOE IPDS 2, ω scans |
| $2\theta_{\max}$, completeness: | 50°, >99% |
| $N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} : | 8390, 1164, 0.055 |
| Criterion for I_{obs} , $N(hkl)_{\text{gt}}$: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 927 |
| $N(\text{param})_{\text{refined}}$: | 116 |
| Programs: | SHELX [1], WinGX [2], DIAMOND [3], PLATON [4] |

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|------------|-------------|----------------------------------|
| C1 | 0.18787(9) | 0.82972(9) | 0.16368(10) | 0.0612(4) |
| H1 | 0.2126(10) | 0.8789(10) | 0.2112(10) | 0.071(4)* |
| C2 | 0.24871(9) | 0.77946(8) | 0.10507(10) | 0.0553(3) |
| H2 | 0.3242(9) | 0.7896(9) | 0.1085(9) | 0.058(3)* |
| C3 | 0.26831(9) | 0.65245(8) | -0.02158(9) | 0.0530(3) |
| H3 | 0.3387(10) | 0.6630(9) | -0.0206(8) | 0.059(3)* |
| C4 | 0.22713(9) | 0.58602(9) | -0.08111(9) | 0.0551(3) |
| H4 | 0.2675(10) | 0.5459(10) | -0.1238(10) | 0.068(4)* |
| C5 | 0.12673(9) | 0.57268(9) | -0.08217(9) | 0.0524(3) |
| H5 | 0.0986(9) | 0.5240(9) | -0.1231(10) | 0.058(3)* |
| C6 | 0.06914(9) | 0.62691(8) | -0.02349(8) | 0.0466(3) |
| H6 | 0.0012(9) | 0.6174(9) | -0.0235(8) | 0.052(3)* |
| C7 | 0.05365(8) | 0.75473(7) | 0.10355(8) | 0.0455(3) |
| C8 | 0.10969(7) | 0.69667(7) | 0.03968(8) | 0.0420(3) |
| C9 | 0.21067(7) | 0.70946(7) | 0.04073(8) | 0.0457(3) |
| N1 | 0.09037(7) | 0.81878(7) | 0.16407(8) | 0.0574(3) |

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Abstract

$C_{18}H_{12}N_2$, tetragonal, $I4_1/a$ (no. 88), $a = 13.8885(6)$ Å, $c = 13.6718(6)$ Å, $V = 2637.2(3)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0295$, $wR_{\text{ref}}(F^2) = 0.0854$, $T = 210$ K.

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The molecular structure of the title compound is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The title compound has been obtained by nickel-catalyzed C–C coupling of 1-chlorisoquinoline [5], which was synthesized by chlorination of isoquinoline-*N*-oxid with POCl₃ [6].

The *N*-oxid was prepared by reaction of isoquinoline with H₂O₂ [7]. Yellow crystals (Mp. 162–163 °C) suitable for single-crystal X-ray diffraction were obtained from diethyl ether by slow evaporation within 3 days.

Experimental details

Coordinates of hydrogen atoms were refined without any constraints or restraints.

Comment

The title compound is a well-known ligand in the coordination chemistry [8–13]. In most complexes 1,1'-bisisoquinoline acts as bidentate ligand, but can also occur as bridging ligand in binuclear complexes. The latter ones are also observed in luminescent silver(I) complexes [14], whereas in gold(I) complexes both types of complexes are formed [15]. Optically active complexes with high chiral recognition can be formed by reaction of 1,1'-bisisoquinoline with chiral palladium complexes [16]. Pd(II) and Ni(II) complexes of 1,1'-bisisoquinolines can be used as catalysts for Suzuki and Heck reactions [17]. 1,1'-Bisisoquinolinium salts exhibit chemiluminescence on addition of hydrogen peroxide in alkaline solution [18].

The title structure shows C₂ symmetry. The asymmetric unit contains half a molecule. Both quinoline moieties are related by a $\bar{4}$ axis, located between the bridging atoms (C7 and C7') running along the crystallographic *c* direction. The quinoline ring system is nearly full planar with a maximal deviation of the best plane of 0.012(1) Å (C1). The length of the C7–C7' bond is 1.496(2) Å. The main structural feature is the position of the quinoline subunits being almost perpendicular to each other [88.54(1)°], which is caused by the transannular steric effect of the hydrogen atoms in the 8-position (labelled here with H6). For enhancing the transannular steric hindrance a series of 8,8'-dialkylsubstituted 1,1-bisisoquinolines were synthesized, whereby dihedral angles between both isoquinoline moieties of 77.68° (Me) and 86.27° (Et) can be observed [19]. Introducing ethoxy substituents in the 4,4'-positions leads to a dihedral angle of 66.20° [20]. During complexation reaction the isoquinoline subunits can be forced into a more planar position depending on the requirements of the metal centre [13]. In presence of other suitable ligands, which also can complete the coordination sphere the twisted bisoquinoline structure is only slightly changed and bisoquinoline often acts as bridging ligand and binuclear complexes are formed [16]. The crystal packing is characterized by a large number of π–π interactions. Furthermore, C–H⋯π interactions are observed [C4–H4⋯C3–C6/C8/C9 ring].

References

- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
- Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
- Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.3.2. Crystal Impact, Bonn, Germany, 2017.
- Spek, A. L.: PLATON – a multipurpose crystallographic tool. *Acta Crystallogr. D* **65** (2011) 148–155.
- Case, F. H.: The preparation of 1,1'- and 3,3'-bisisoquinoline. *J. Org. Chem.* **17** (1952) 471–472.
- Alcock, N. W.; Brown, J. M.; Hulmes, D. I.: Synthesis and resolution of 1-(2-diphenylphosphino-1-naphthyl)isoquinoline; a P–N chelating ligand for asymmetric catalysis. *Tetrahedron Asymmetry* **4** (1993) 743–756.
- Zhu, C.; Yi, M.; Wei, D.; Chen, X.; Wu, Y.; Cui, X.: Copper-catalyzed direct amination of quinoline *N*-oxides via C–H bond activation under mild conditions. *Org. Lett.* **16** (2014) 1840–1843.
- Starke, I.; Kammer, S.; Grunwald, N.; Schilde, U.; Holdt, H.-J.; Kleinpeter, E.: Complexation of diazaperylene and bisoquinoline with transition metal ions in the gas phase studied by electrospray ionization mass spectrometry. *Rapid Commun. Mass Spectrom.* **22** (2008) 665–671.
- Frediani, P.; Giannelli, C.; Salvini, A.; Ianelli, S.: Ruthenium complexes with 1,1'-bisisoquinoline as ligand. Synthesis and hydrogenation activity. *J. Organomet. Chem.* **667** (2003) 197–208.
- Yu, W.-Y.; Cheng, W.-C.; Che, C.-M.; Wang, Y.: Synthesis, redox properties and reactivities of ruthenium(II) complexes of 1,1'-bisisoquinoline (BIQN) and X-ray crystal structure of [Ru^{II}(terpy)(BIQN)(Cl)]ClO₄ (terpy = 2,2':6',2''-terpyridine). *Polyhedron* **13** (1994) 2963–2969.
- Yang, R.; Dai, L.: Synthesis and electronic spectra of ruthenium(II)-1,1'-bisisoquinoline complexes. *Chin. Chem. Lett.* **4** (1993) 1021–1024.
- Cheng, L. K.; Yeung, K. S.; Che, C. M.; Cheng, M. C.; Wang, Y.: X-ray structure and spectroscopic properties of platinum(II) complexes of 1,1'-bisisoquinoline. *Polyhedron* **12** (1993) 1201–1207.
- Ashby, M. T.; Alguindigue, S. S.; Schwane, J. D.; Daniel, T. A.: Regular and inverse secondary kinetic enthalpy effects (KHE) for the rate of inversion of thioether and 1,1'-bisisoquinoline complexes of ruthenium and osmium. *Inorg. Chem.* **40** (2001) 6643–6650.
- Bardaji, M.; Miguel-Coello, A. B.; Espinet, P.: Predominance of bridging coordination in luminescent 1,1'-bisisoquinoline silver(I) derivatives. *Inorg. Chim. Acta* **386** (2012) 93–101.
- Bardaji, M.; Miguel-Coello, A. B.; Espinet, P.: Mono- and dinuclear luminescent 1,1'-bisisoquinoline gold(I) complexes. *Inorg. Chim. Acta* **392** (2012) 91–98.
- Dai, L.-X.; Zhou, Z.-H.; Zhang, Y.-Z.; Ni, C.-Z.; Zhang, Z.-M.; Zhou, Y.-F.: 1,1'-Bi-isoquinoline: a chiral bidentate *N*-donor ligand with C₂-symmetry; formation of optically active complexes with high chiral recognition. *J. Chem. Soc. Chem. Commun.* (1987) 1760–1762.
- Khrushcheva, N. S.; Bulygina, L. A.; Starikova, Z. A.; Sokolov, V. I.: Synthesis, structure, and catalytic activity of

- complexes of 1,1'-bisoquinoline with PdCl₂ and NiCl₂. Russ. Chem. Bull. **63** (2014) 883–889.
18. Maeda, K.; Matsuyama, Y.; Isozaki, K.; Yamada, S.; Mori, Y.: Mechanism of the chemiluminescence of bisoquinolinium salts. J. Chem. Soc. Perkin Trans. **2** (1996) 121–126.
19. Tsue, H.; Fujinami, H.; Itakura, T.; Tsuchiya, R.; Kobayashi, K.; Takahashi, H.; Hirao, K.: Absolute configuration of 8,8'-dialkyl-1,1'-bisoquinoline. Chem. Lett. **28** (1999) 17–18.
20. Kapatsina, E.; Mateescu, M.; Baro, A.; Frey, W.; Laschat, S.: Concise synthesis of [1,1'-bisoquinoline]-4,4'-diol *via* a protecting group strategy and its application for potential liquid-crystalline compounds. Helvet. Chim. Acta **92** (2009) 2024–2037.