SHORT PAPER

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Synthesis and crystal structure of 2,2′-dimethyl-8,8′-biquinolyl[†]

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2,2′-Dimethyl-8,8′-biquinolyl was prepared by homo-coupling and its structure was first elucidated by X-ray analysis.

The stereochemistry of 1,1′-binaphthyl system has retained special attention due to the atropisomerism. The molecular structure of racemic[1] and optically active[2] 1,1′-binaphthyl has been determined by X-ray crystallography. On the other hand, the structure of 8,8′-biquinolyl isoelectronic with 1,1′-binaphthyl has not been elucidated by X-ray determination. The length of the inter-ring C–C bond, the interplanar dihedral angle and the isolation of atropisomers by chemical modification of 1,1′-binaphthyl with nitrogen is of great interest. In order to provide the structural information of 2,2′-disubstituted 8,8′-biquinolyl that is available by homo-coupling reacton, we report first the crystal structure of racemic 2,2′-dimethyl-8,8′-biquinolyl .

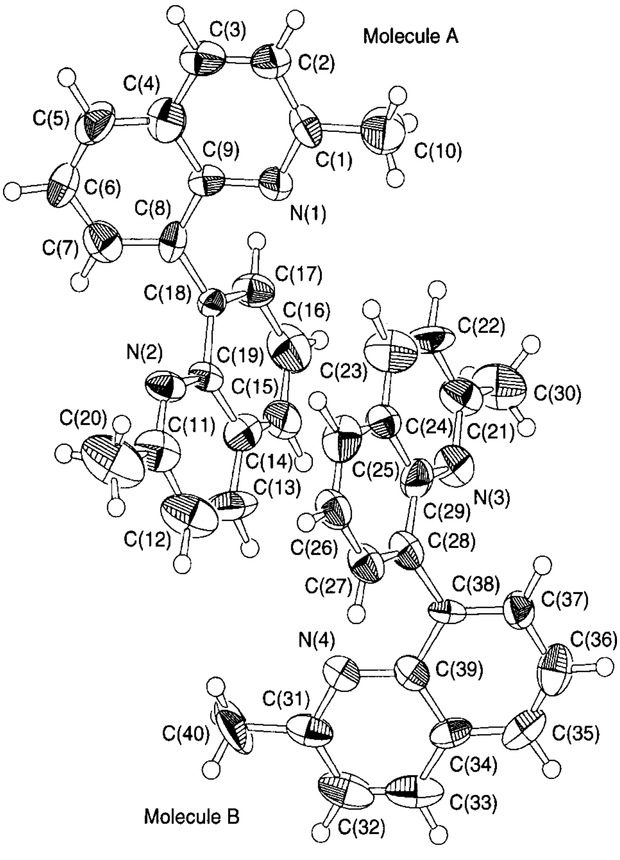

Fig. 1 Crystal structure of 2,2′-dimethyl-8,8′-biquinolyl 3.

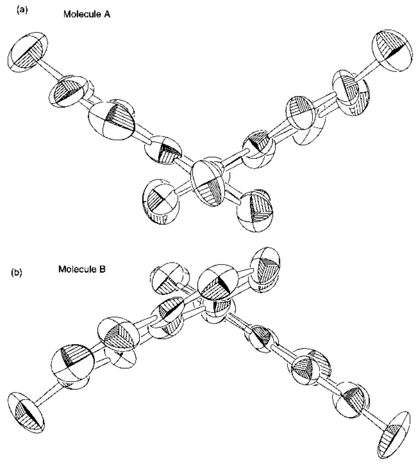

Fig. 2 Molecular sturctures showing side view (a) down the C(18)–C(8) direction and (b) down the C(28)–C(38) direction.

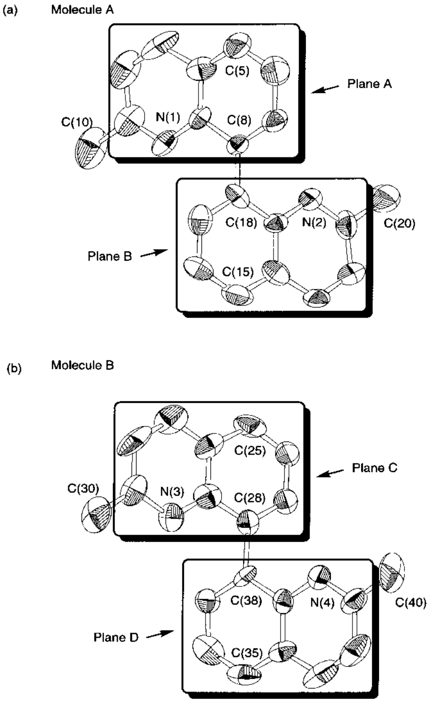

Fig. 3 Schematic representation of quinoline planes.

Scheme 1

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[†] This is a Short Crystallographic Paper

The title compound **3** was synthesized in a two step reaction as shown in Scheme 1. Triflate **2** was prepared from commercially available 2-methyl-8-quinolinol **1** and Tf_2O in pyridine quantitatively.[3] Ni(0) catalyst was *in-situ* generated and subsequently used for homo-coupling reaction. The molar ratio **2** : $NiCl_2$: Zn : NaI : PPh_3 = 1 : 0.25 : 2.5 : 1 : 1 in dried DMF at 90 °C gave a homo-coupling product **3** in 65% yield.[4]

The structure analysis shows that, in the crystal, the asymmetric unit contains two independent molecules A and B (Fig. 1), although there is pseudo-symmetry between the molecules A and B.[5] The molecules exists in a *transoid* conformation in contrast with a *cisoid* conformation with a angle of 68˚ of racemic 1,1′-binaphthyl.[1] The main differences between the two molecules are in the conformation of the quinoline rings. It is confirmed that the molecule B is slightly deformed compared with the molecule A (Fig. 2). The torsion angles between quinoline planes are 116.3˚ in the molecule A (Fig. 2a) and 118.5˚ in the molecule B (Fig. 2b). Although the quinoline rings are planar, in the molecule A, the C(8) and C(18) atoms deviate by 0.09 and 0.18 Å from the planes B and A, respectively (Fig. 3a). Further, in the molecule B, C(28) and C(38) atoms deviate by 0.18 and 0.23 Å from the planes D and C, respectively (Fig. 3b). These information indicates that the intramolecular quinoline rings are slightly tilted to each other and that both the atoms C(5), C(8), C(18) and C(15) and the atoms C(25), C(28), C(38) and C(35) are not colinear. The torsion angles, which are close to perpendicular, mean the reduction of π-delocalization between the two quinoline rings. The methyl atoms C(10), C(20), C(30) and C(40) deviate by 0.17, 0.03, 0.16 and 0.09 Å from planarity, respectively. The lengths of the linking bond between quinoline rings are 1.47 Å in the molecule A and 1.52 Å in the molecule B. The former nearly corresponds to the length of 1.475 Å between two naphthalenes of *transoid R*-1,1′-binaphthyl (torsion angle θ = 103˚).[2] On the other hand, the molecule B has a relatively long length between quinoline rings, indicating more single bond character compared with the molecule A. It is anticipated that the molecule **3** is not crowded around the linking bond in comparison with 1,1′-binaphthyl, therefore the isolation of optically active 8,8′-biquinolyl will be difficult because of low energy barrier for rotation as reported by Bell.[6]

Experimental

Melting points were determined on a Yanaco Melting Point apparatus and are uncorrected. IR spectra were taken on a JASCO FT/IR-5M spectrometer (KBr pellets). ^1H and ^{13}C spctra were recorded on either a JEOL JNM-EX270 or a Bruker DRX500 spectrometer. MS spectra were obtained on a Shimadzu QP-1000EX. High resolution MS spectra were obtained on a Shimadzu Kratos Concept 1s mass spectrometer. Column chromatography was performed using Wakogel C300 silica gel. All reactions were performed under nitrogen.

Preparation of triflate **2**: To a solution of 2-methyl-8-quinolinol **1** (796 mg, 5.0 mmol) in dried pyridine (4 ml) at 0 °C was slowly added trifluoromethanesulfonic anhydride 1.0 ml (1.69 g, 6.0 mmol). The resulting mixture was allowed to warm up to rt and stirred for 3 h. The mixture was poured into water and extracted with chloroform. The organic layer was washed with 1*N* HCl and water, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, column chromatography with haxane-EtOAc (2:1) afforded **2** as a white solid (1.44 g, 99%), mp 54–56 °C. IR: ν^{max}/cm^{-1} (KBr) 1604, 1502, 1472, 1249, 1326, 1208, 764; ^1H NMR (270 MHz, $CDCl_3$): δ 2.80 (s, 3H, CH_3), 7.40 (d, *J* = 8.6 Hz, 1H, 3-quiH), 7.49 (dd, *J* = 7.6, 7.9 Hz, 1H, 6-quiH), 7.58 (dd, *J* = 1.3, 7.6 Hz, 1H, 7-quiH), 7.80 (dd, *J* = 1.3, 7.9 Hz, 1H, 5-quiH), 8.01 (d, *J* = 8.6 Hz, 1H, 4-quiH); m/z (EI) 130 (100%), 158 (58), 291 (M^+, 21). (Found: C, 2.70; H, 45.22. $C_{11}H_8F_3NO_3S$ requires C, 2.77; H, 45.36%).

Preparation of biquinoline **3**: A mixture of zinc dust (163 mg, 2.5 mmol), sodium iodide (150 mg, 1.0 mmol), triphenylphosphine (262 mg, 1.0 mmol), and nickel(II) chloride in dried DMF (6 ml) was stirred at 60 °C for 30 min. Then the mixture darkened and Ni(0) was generated. To the dark mixture 2-methyl-8-quinolyl triflate **2** (291 mg, 1.0 mmol) was added and the mixture was stirred at 90 °C for 1 h. After the reaction had been completed (monitored by TLC), the mixture was filtered and washed with diethyl ether. The filtrate and washings were poured into water and extracted with diethyl ether. The organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, column chromatography with benzene-EtOAc (2:1) afforded the title compound **3** as a white solid (92 mg, 65%), mp 150–151 °C. IR: ν_{max}/cm^{-1} (KBr) 2959, 1601, 1497, 1197, 761; ^1H NMR (500 MHz, $CDCl_3$): δ 2.52 (s, 6H, $2CH_3$), 7.23 (d, *J* = 8.6 Hz, 2H, 3,3′-biquiH), 7.58 (dd, *J* = 6.9, 8.1 Hz, 2H, 6,6′-biquiH), 7.82 (dd, *J* = 1.2, 8.1 Hz, 2H, 5,5′-biquiH), 7.88 (dd, *J* = 1.2, 6.9 Hz, 2H, 7,7′-biquiH), 8.08 (d, *J* = 8.6 Hz, 2H, 4,4′-biquiH); ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.62, 121.49, 124.74, 126.81, 127.09, 132.76, 136.08, 137.94, 146.69, 158.21; *m/z* (EI) 283 (100%), 284 (M^+, 71); M^+ at *m/z* 284.13052 (calc. for $C_{20}H_{16}N_2O_2$, 284.13135).

Crystal data **3**: $C_{20}H_{16}N_2$, M_r = 284.36, orthorhombic, Pna2_1, a = 20.875(3), b = 8.769(3), c = 17.131(3) Å, V = 3136(1) Å^3, D_x = 1.205 g cm^{-3}, Z = 8, μ = 0.71 cm^{-1}, T = 296K. A colorless prism prepared by slow evaporation from chloroform-hexane was used for data collection with a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å) from a rotating-anode generator oprating at 50 kV and 200 mA. Cell constants and an orientation matrix for data collection, obtained form a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $23.6 < 2\theta < 29.0˚$. A total of 4073 reflections were collected. The intensities of three representative reflections were measured after every 150 reflections and showed no significant intensity variation during the data collection. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[7] and expanded using Fourier technique.[8] Space group Pnma was considered but was ultimately rejected in favour of Pna2^1. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2097 observed reflections ($I > \sigma(I)$) and 396 variable parameters and converged with R = 0.077 and R^w = 0.066. All calculations were performed with the teXsan for windows.[9] Full crystallographic details will be deposited at the Cambridge Crystallographic Data Centre (CDDC).

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References

1 K. A. Kerr and J. M. Robertson, *J. Chem. Soc. (B)*, 1969, 1146.
2 R. Kuroda and S. F. Mason, *J. Chem. Soc. Perkin Trans. 2*, 1981, 167.
3 A. M. Echavarren and J. K. Stille, *J. Am. Chem. Soc.*, 1987, **109**, 5478.
4 J. Yamashita, Y. Inoue, T. Kondo and H. Hashimoto, *Chem. Lett.*, 1986, 407.
5 Although it seems that the crystal structure has an intermolecular symmetry, the symmetry check program showed no inversion center.
6 F. Bell and W. H. D. Morgan, *J. Chem. Soc.*, 1950, 1963.
7 SIR92: A. Altomare, M. C. Burla, M. Camalli, M. Cascaramp. M., C. Giacovazzao, A. Guagliardi and G. Polidori, *J. Appl. Cryst.*, 1994, **27**, 435.
8 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
9 teXsan for windows: Crystal Structure Analysis Package, Molecular Structure Corporation, 1997.