

- KAROLAK-WOJCIECHOWSKA, J., KWIATKOWSKI, W. & KIEĆ-KONONOWICZ, K. (1989). *Acta Cryst.* **C45**, 1467–1469.
- KAROLAK-WOJCIECHOWSKA, J. & KIEĆ-KONONOWICZ, K. (1991). In preparation.
- KIEĆ-KONONOWICZ, K., ZEJC, A., MIKOŁAJCZYK, M., ZATORSKI, A., KAROLAK-WOJCIECHOWSKA, J. & WIECZOREK, M. (1980). *Tetrahedron*, **36**, 1079–1087.
- KIEĆ-KONONOWICZ, K., ZEJC, A., MIKOŁAJCZYK, M., ZATORSKI, A., KAROLAK-WOJCIECHOWSKA, J. & WIECZOREK, M. (1981). *Tetrahedron*, **37**, 409–415.
- KIEĆ-KONONOWICZ, K., ZATORSKI, A. & KAROLAK-WOJCIECHOWSKA, J. (1989). *Phosphorus Sulfur Silicon*, **42**, 191–199.
- KOLASA, K., KLEINROK, Z., PIETRUSIEWICZ, T., CZECHOWSKI, G., KIEĆ-KONONOWICZ, K. & ZEJC, A. (1989). *Pol. J. Pharmacol. Pharm.* **41**, 377–382.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

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## Structure of (*R*)-*N,N,N',N'*-Tetramethyl-[1,1'-binaphthalene]-2,2'-diamine

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**Abstract.**  $C_{24}H_{24}N_2$ ,  $M_r = 340.5$ , tetragonal,  $I4_1$ ,  $a = 11.872$  (2),  $c = 13.746$  (3) Å,  $V = 1937.5$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.17$  g cm<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.63$  cm<sup>-1</sup>,  $F(000) = 728$ , room temperature,  $R = 0.043$  for 736 reflections with  $I > 3\sigma(I)$ . The dihedral angle between the planes of the naphthyl rings is  $71.2(1)^\circ$ . The N atoms in the dimethylamino groups are almost  $sp^2$  hybridized.

**Introduction.** Structural studies on  $C_2$ -symmetric 1,1'-binaphthyl compounds have received a great deal of attention in the last few years owing to their relevance in asymmetric synthesis (Noyori & Takaya, 1985; Noyori, 1989). Their conformation has been studied in solution by optical methods like circular-dichroism spectroscopy (Mason, Seal & Roberts, 1974) and liquid-crystal techniques (Gottarelli, Spada, Bartsch, Solladiè & Zimmermann, 1986), and in the solid state by X-ray analysis (Akimoto & Iitaka, 1969; Harata & Tanaka, 1973; Kuroda & Mason, 1981; Pauptit & Trotter, 1981, 1983). We report here the molecular structure of (*R*)-*N,N,N',N'*-tetramethyl-[1,1'-binaphthalene]-2,2'-diamine, a new 1,1'-binaphthyl compound whose potential as a chiral ligand is now being investigated (Salvadori, Rosini & Franzini, in preparation).

**Experimental.** The title compound was prepared from (*R*)-[1,1'-binaphthalene]-2,2'-diamine according to the method described by Benson, Cai, Colon,

Haiza, Tokles & Snyder (1988). Pyramidal (101) yellow crystals were obtained by recrystallization from toluene. A crystal, dimensions  $ca 2 \times 1 \times 0.5$  mm, was chosen for the intensity data collection which was carried out on an Ital Structures four-circle automatic diffractometer using graphite-monochromated  $Mo K\alpha$  radiation. Preliminary Weissenberg photographs showed Laue symmetry and systematic absences consistent with space group  $I4_1$ . The unit-cell parameters were derived through least-squares fitting of  $2\theta$  values of 30 reflections ( $13 < \theta < 21^\circ$ ). 1876 reflections measured with  $3 \leq \theta \leq 25^\circ$ ,  $h 0$  to 14,  $k 0$  to 14,  $l - 16$  to 16,  $\omega$ -scan mode, scan width  $1.6^\circ$ , scan speed  $2.5^\circ \text{ min}^{-1}$ ; no significant variation in the intensity of one reflection (226) monitored every 60 measurements; Lorentz and polarization corrections; Friedel opposites merged neglecting the contribution of anomalous scattering, thus obtaining a set of 736 unique reflections with  $I > 3\sigma(I)$ ; absorption correction by *DIFABS* (Walker & Stuart, 1983), correction factors in the range 0.78–1.14. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined on *F* with *SHELX76* (Sheldrick, 1976). The atomic scattering factors were those incorporated in *SHELX76*. Final  $R = 0.043$ ,  $wR = 0.033$  [ $w = 1/\sigma(F_o)^2$ ],  $S = 4.76$ . Anisotropic thermal parameters for all non-H atoms, methyl H-atom positions constrained using the AFIX option of *SHELX76*; 147 variables, max.  $\Delta/\sigma$  in the final least-squares cycle

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

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

	x	y	z	$U_{eq}$
C(1)	-0.0300 (3)	0.4448 (3)	0.0814 (4)	0.039 (1)
C(2)	-0.1066 (3)	0.4195 (3)	0.0093 (4)	0.046 (2)
C(3)	-0.1548 (3)	0.3097 (4)	0.0050 (4)	0.049 (2)
C(4)	-0.1293 (4)	0.2300 (4)	0.0721 (4)	0.048 (2)
C(5)	-0.0277 (4)	0.1699 (4)	0.2182 (4)	0.050 (1)
C(6)	0.0472 (4)	0.1924 (4)	0.2910 (5)	0.057 (2)
C(7)	0.0999 (4)	0.2983 (4)	0.2955 (4)	0.053 (2)
C(8)	0.0760 (3)	0.3795 (4)	0.2285 (4)	0.045 (2)
C(9)	-0.0027 (3)	0.3604 (3)	0.1521*	0.037 (1)
C(10)	-0.0528 (3)	0.2522 (3)	0.1474 (4)	0.039 (1)
N	-0.1381 (3)	0.5002 (3)	-0.0608 (3)	0.066 (1)
C(11)	-0.1960 (6)	0.5986 (5)	-0.0294 (5)	0.107 (3)
C(12)	-0.1722 (9)	0.4607 (6)	-0.1565 (4)	0.143 (4)

\* Held fixed to define the origin.

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

C(1)—C(1)'	1.492 (5)	C(5)—C(10)	1.411 (7)
C(1)—C(2)	1.378 (7)	C(6)—C(7)	1.406 (7)
C(1)—C(9)	1.433 (5)	C(7)—C(8)	1.363 (7)
C(2)—C(3)	1.423 (6)	C(8)—C(9)	1.424 (5)
C(2)—N	1.409 (6)	C(9)—C(10)	1.417 (5)
C(3)—C(4)	1.356 (7)	N—C(11)	1.422 (7)
C(4)—C(10)	1.402 (7)	N—C(12)	1.454 (7)
C(5)—C(6)	1.365 (8)		
C(1)′—C(1)—C(2)	120.4 (4)	C(7)—C(8)—C(9)	121.5 (4)
C(1)′—C(1)—C(9)	120.4 (3)	C(1)—C(9)—C(8)	122.5 (2)
C(2)—C(1)—C(9)	119.0 (3)	C(1)—C(9)—C(10)	120.5 (3)
C(1)—C(2)—C(3)	119.6 (4)	C(8)—C(9)—C(10)	117.0 (3)
C(1)—C(2)—N	121.2 (3)	C(4)—C(10)—C(5)	121.1 (4)
C(3)—C(2)—N	119.1 (4)	C(4)—C(10)—C(9)	118.4 (3)
C(2)—C(3)—C(4)	121.4 (4)	C(5)—C(10)—C(9)	120.5 (3)
C(3)—C(4)—C(10)	121.0 (4)	C(2)—N—C(11)	118.6 (4)
C(6)—C(5)—C(10)	120.5 (4)	C(2)—N—C(12)	118.2 (4)
C(5)—C(6)—C(7)	119.8 (5)	C(11)—N—C(12)	113.9 (5)
C(6)—C(7)—C(8)	120.7 (5)		

0.06 for non-H atoms; max. and min. heights in the final difference Fourier synthesis 0.14 and  $-0.14 \text{ e \AA}^{-3}$ .

**Discussion.** The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.\* An ORTEPII (Johnson, 1976) drawing of the molecule with atom labelling is shown in Fig. 1. Bond lengths and bond angles are listed in Table 2; geometrical calculations were performed using PARST (Nardelli, 1983). The asymmetric unit is half of the molecule; the other half is generated by rotation around a twofold axis which bisects the C(1)—C(1)' bond. The bond lengths and bond angles within the naphthyl group are in agreement with

\* Lists of structure factors, anisotropic thermal parameters for non-H atoms, and positional and thermal parameters for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53623 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

those found in naphthalene and its derivatives. The naphthalene rings are essentially planar, the largest displacement of any non-H atom from the least-squares plane being 0.017 (5)  $\text{\AA}$ . The maximum torsion angle within the naphthalene ring is 2.3 (6) $^\circ$ , the average value is 0.9 (7) $^\circ$ . The distance of the N atom from the least-squares plane is 0.049 (4)  $\text{\AA}$ . The methyl groups are positioned on opposite sides of the naphthalene plane and their orientation can be defined by the torsion angles C(3)—C(2)—N—C(11) [116.0 (5) $^\circ$ ] and C(3)—C(2)—N—C(12) [ $-28.7$  (7) $^\circ$ ]. The values of the three angles C(2)—N—C(11), C(2)—N—C(12) and C(11)—N—C(12) indicate the prevailing  $sp^2$  hybridization of the N atoms. The dihedral angle between the two naphthyl groups is 71.2 (1) $^\circ$  (Fig. 2). This is the smallest dihedral angle among those measured in optically active 1,1'-binaphthyl compounds whose values range from 77 $^\circ$  for (+)-2,2'-dihydroxy-[1,1'-binaphthalene]-3,3'-dicarboxylic acid dimethyl ester bromobenzene solv-

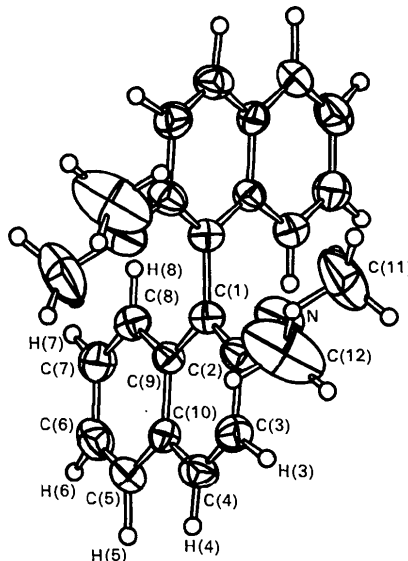


Fig. 1. ORTEPII (Johnson, 1976) drawing of the title compound with the atom-labelling scheme.

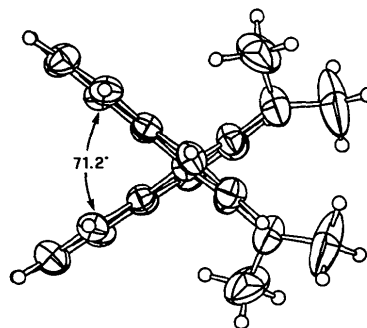


Fig. 2. View of the molecule showing the angle between the two naphthalene rings.

ate to  $103^\circ$  for (-)-1,1'-binaphthyl (Akimoto & Iitaka, 1969; Harata & Tanaka, 1973; Kuroda & Mason, 1981; Paupit & Trotter, 1981, 1983). The present dihedral angle is comparable to that [ $74.4(2)^\circ$ ] found in [(*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene] (8,9,10-trinorborna-2,5-diene)-rhodium(I) perchlorate (Toriumi, Ito, Takaya, Souchi & Noyori, 1982) where the binaphthyl derivative is coordinated to the metal atom.

As previously shown (Harata & Tanaka, 1973), bulky substituents at the 2,2' positions give rise to large dihedral angles. However, in this case the twist observed between the plane of each  $N(CH_3)_2$  and the plane of the corresponding naphthalene ring can constitute a more efficient way of reducing the steric repulsion than the increase of the dihedral angle between the two naphthalenic rings, also taking into account that for large dihedral angles steric repulsion between an  $N(CH_3)_2$  group of a naphthalene moiety and the other aromatic ring can become important.

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## References

- AKIMOTO, H. & IITAKA, Y. (1969). *Acta Cryst.* **B25**, 1491–1500.  
 BENSON, S. C., CAI, P., COLON, M., HAIZA, M. A., TOKLES, M. & SNYDER, J. K. (1988). *J. Org. Chem.* **53**, 5335–5341.  
 GOTTARELLI, G., SPADA, G. P., BARTSCH, R., SOLLADIÈ, G. & ZIMMERMANN, R. (1986). *J. Org. Chem.* **51**, 589–592.  
 HARATA, K. & TANAKA, J. (1973). *Bull. Chem. Soc. Jpn.* **46**, 2747–2751.  
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 KURODA, J. & MASON, F. (1981). *J. Chem. Soc. Perkin Trans. 2*, pp. 167–170.  
 MASON, S. F., SEAL, R. H. & ROBERTS, D. R. (1974). *Tetrahedron*, **30**, 1671–1682.  
 NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.  
 NOYORI, R. (1989). *Chem. Soc. Rev.* **18**, 187–208.  
 NOYORI, R. & TAKAYA, H. (1985). *Chem. Scr.* **25**, 83–89.  
 PAUPTIT, R. A. & TROTTER, J. (1981). *Can. J. Chem.* **59**, 1149–1152.  
 PAUPTIT, R. A. & TROTTER, J. (1983). *Can. J. Chem.* **61**, 69–71.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 TORIUMI, K., ITO, T., TAKAYA, H., SOUCHI, T. & NOYORI, R. (1982). *Acta Cryst.* **B38**, 807–812.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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## Structure of a Chiral Amide Derived from a (Vinylketenimine)tricarbonyliron(0) Complex

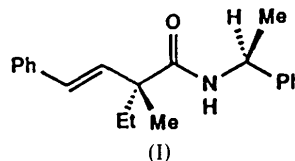
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**Abstract.** (2*R*)-2-Ethyl-2-methyl-4-phenyl-*N*-[(*S*)-1-phenylethyl]-(*E*)-3-butenamide,  $C_{21}H_{25}NO$ ,  $M_r = 307.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.071(7)$ ,  $b = 19.218(15)$ ,  $c = 19.406(14)$  Å,  $V = 3756$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.09$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(Mo K\alpha) = 0.6$  cm<sup>-1</sup>,  $F(000) = 1328$ ,  $T = 290$  K,  $R = 0.063$  for 1600 unique observed [ $I/\sigma(I) \geq 2.0$ ] reflections. The two independent molecules show significant conformational differences, principally involving the (C=O)—C bond adjacent to the amide group. The molecules are linked into chains by N—H...O hydrogen bonds.

**Introduction.** The reaction of a homochiral (vinylketenimine)tricarbonyliron(0) complex with ethyl-

lithium has been shown to produce only one diastereoisomer of the  $\beta,\gamma$ -unsaturated amide (I) in >95% purity (Alcock, Pike, Richards & Thomas, 1990). The crystal structure of this amide has been determined to establish the stereospecificity of the reaction. (-)-(*S*)- $\alpha$ -Methylbenzylamine was used as the starting material for the preparation of the iron complex and the retained chiral centre provided a reference point for identifying the chirality of the new quaternary carbon centre formed in the reaction.



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