The Crystal and Molecular Structure of *R*-(−)-1,1′-Binaphthyl: the Conformational Isomerism and a Comparison of the Chiral with the Racemic Packing Mode

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The molecular and crystal structure of *R*-(−)-1,1′-binaphthyl has been determined from single-crystal *X*-ray data and refined by least-squares methods to *R* 0.045. The tetragonal crystal has unit-cell dimensions, a = 7.212 6(9), c = 27.510(5) Å, space group $P4_12_12$, and Z = 4. The molecule has a transoid conformation in the active crystal with a dihedral angle of 103° between the mean molecular planes of the two naphthalene residues. The packing modes of the molecules in the active and in the more dense (9.4%) racemic crystal are compared in connection with the spontaneous optical resolution of 1,1′-binaphthyl by crystallisation at temperatures above 76°.

THE present work reports an *X*-ray diffraction determination of the crystal and molecular structure of *R*-(−)-1,1′-binaphthyl. The molecular and crystal structure of racemic 1,1′-binaphthyl was determined by Kerr and Robertson,[1] following a previous preliminary study,[2] and the demonstration that 1,1′-binaphthyl crystallizes in at least two distinct forms.[3] The forms are characterised by differences in the m.p. and in the i.r. spectrum of microcrystalline mulls.[3] The racemic crystal, m.p. 145°, gives a diagnostic strong i.r. band at 769 cm^{-1}, together with other features which have no counterpart, or are weak, in the corresponding i.r. spectrum of the optically active crystal, m.p. 158°. The spectroscopic differences suggest [3] that 1,1′-binaphthyl, with a cisoid conformation in the racemic crystal,[1,2] has a transoid conformation in the active crystal.

The investigation of the molecular conformation of 1,1′-binaphthyl in the active crystal was a principal aim of the present study, the second main objective being a comparison of the respective molecular packing modes in the active and in the racemic crystal. Thermodynamically the racemic crystal is the more stable up to a transition temperature [4] at 76°. Above the transition temperature the racemic crystals undergo a solid-state transformation to a conglomerate of active crystals, and crystallization from the melt at 150° similarly affords a mixture of crystals which individually contain solely the *R*-(−)- or the *S*-(+)-isomer.[4]

The majority of racemates crystallize from solution or from the melt in lattices with inversion site symmetry, the inversion centre relating the two optical antipodes of the racemate. A statistical analysis of the *X*-ray structures of *ca.* 900 racemates shows that some 70% crystallize in the space groups, $P\bar{1}$, $P2_1/c$, and $C2/c$, all with inversion site symmetry.[5] Only 250 cases have been identified, including 1,1′-binaphthyl, of racemates which, under given conditions, crystallize into a conglomerate of enantiomorphous active crystals, each containing a single enantiomer.[6] The principal method for the large-scale optical resolution of racemates is entrainment, the seeding of a melt or supersaturated solution of the racemate with a crystal of one of the enantiomers, and the procedure is confined to the minor class of racemates which spontaneously resolve on crystallization into a conglomerate of active single crystals.[7] The investigation of the molecular packing modes in examples of the minor class of self-resolving racemates is relevant to extensions of the entrainment method which, with other resolution procedures, has an enantioselective importance in pharmacological and other biological applications of synthetic racemates.[8]

EXPERIMENTAL

Racemic 1,1′-binaphthyl (Eastman Kodak) was heated in a loosely stoppered Pyrex tube at 180° (15 min) to remove all crystal seeds. After brief contact with a pointed chip of dry-ice to produce a seed, the tube was maintained at 150° in a thermostat. The crystals formed after two days were separated and the absorption and c.d. spectra of fragments from ten individual large crystals were measured. Eight of the crystals contained the *R*-(−)-enantiomer and the other two were composed of the *S*-(+)-antipode. The fragment from the *R*-(−)-crystal selected for the *X*-ray diffraction study was optically pure since the c.d. spectrum was quantitatively enantiomorphous to that recorded [9] for the *S*-(+)-isomer prepared by the deamination of *S*-(+)-4,4′-diamino-1,1′-binaphthyl.

The *R*-(−)-crystal employed for the *X*-ray diffraction study had the dimensions, 0.16 × 0.23 × 0.36 mm. Unit cell dimensions were determined from Weissenberg photographs and were subsequently refined on a diffractometer.

Crystal Data.—$C_{20}H_{14}$, $M = 254.3$. Tetragonal, a = 7.212 6(9), c = 27.510(5) Å, U = 1 431.1 Å^3, D_m = 1.18, Z = 4, D_c = 1.180 g cm^{-3}, $F(000)$ = 536, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 4.35 cm^{-1}, space group $P4_12_12$.

In contrast, the racemic 1,1′-binaphthyl crystal [1] is monoclinic, a = 20.98, b = 6.35, c = 10.13 Å, β = 105.17°, space group $C2/c$, Z = 4, with a smaller unit cell volume, U = 1 302.3 Å^3, and a correspondingly larger density, D_c = 1.297 g cm^{-3}. The racemic and the optically active crystals of 1,1′-binaphthyl are separated by a 30% aqueous solution of potassium bromide (density 1.23 g cm^{-3}).

The *R*-(−)-crystal intensities were measured with Cu-K_α radiation on an Enraf–Nonius CAD4 automated diffractometer operated in the θ—2θ scan mode up to θ = 60°. Out of the 1061 unique reflections observed, 731 with $|F_o| \geqslant 3\sigma$ were used for the refinement. The intensity data were not corrected for absorption.

Structure Determination.—The structure was solved by the direct method with the use of MULTAN 78 and was subsequently refined employing SHELX 76. The atomic scattering factors for the carbon and the hydrogen atoms were taken from refs. 10 and 11, respectively. All the hydrogen atoms appeared in the difference Fourier map and these atoms were included in the refinement. Anisotropic and isotropic thermal factors were adopted for the carbon and for the hydrogen atoms, respectively. The final *R* value was 0.045. Observed and calculated structure amplitudes and the thermal parameters of the atoms are tabulated in Supplementary Publication No. SUP 22929 (4 pp.).*

DISCUSSION

Table 1 lists the final set of atomic co-ordinates obtained for *R*-(—)-1,1′-binaphthyl in the active crystal, and Figure 1 gives the corresponding molecular bond lengths and bond angles. The molecular conformation of 1,1′-binaphthyl is transoid in the active crystal, with a dihedral angle between the mean planes of the two naphthalene nuclei of 103°, compared with a corresponding angle[1] of 68° for the cisoid conformation of the molecule in the racemic crystal. The inference[3] from the microcrystalline mull i.r. spectra of a molecular conformational change from cisoid in the racemic to transoid in the active crystal is thus confirmed.

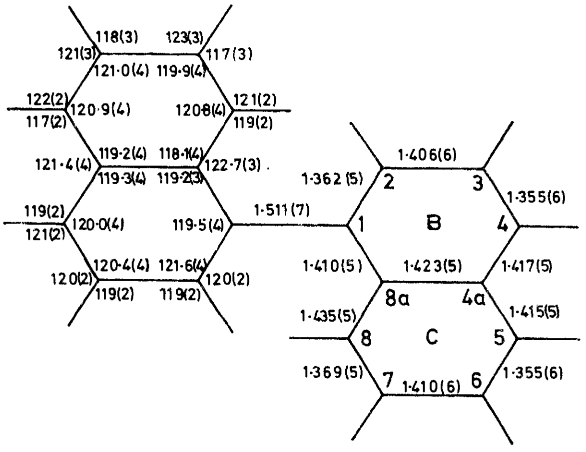

FIGURE 1 The dimensions of 1,1′-binaphthyl in the *R*-(—)-crystal

TABLE 1

Fractional atomic co-ordinates (× 10^4 for carbon and × 10^3 for hydrogen atoms) with estimated standard deviations in parentheses.

	x	*y*	*z*
C(1)	1 266(5)	150(5)	2 420(1)
C(2)	2 916(6)	330(6)	2 656(2)
C(3)	4 245(6)	1 643(7)	2 510(2)
C(4)	3 933(6)	2 735(7)	2 118(2)
C(4a)	2 243(5)	2 585(6)	1 858(1)
C(5)	1 892(7)	3 677(7)	1 441(2)
C(6)	283(6)	3 500(6)	1 191(2)
C(7)	−1 102(7)	2 249(6)	1 344(2)
C(8)	−816(5)	1 168(6)	1 745(1)
C(8a)	888(5)	1 279(5)	2 013(1)
H(2)	320(5)	−48(5)	295(1)
H(3)	544(6)	168(6)	268(1)
H(4)	487(6)	361(5)	201(1)
H(5)	294(6)	467(6)	134(1)
H(6)	7(6)	419(6)	87(1)
H(7)	−227(8)	303(6)	116(2)
H(8)	−180(4)	322(4)	187(1)

Other structural dimensions of 1,1′-binaphthyl in the active crystal do not differ appreciably from the corresponding measures for the molecule in the racemic crystal, with the exception of the exocyclic C(1)–C(1′) bond which is significantly longer [1.511(7) Å] than the corresponding bond[1] (1.475 Å) of the cisoid racemate conformation. The difference between the lengths of the C(1)–C(1′) bond in the two crystal conformations is too large to arise primarily from the reduced π-delocalisation between the two naphthalene moieties in the transoid conformer where the dihedral angle is the closer to π/2. The difference between the dihedral angle of the two crystal conformers is, however, the main factor governing the change with conformation of the intramolecular distance between a given atom of one naphthalene nucleus and a particular non-bonded atom of the other nucleus in 1,1′-binaphthyl (Table 2). While the closest intramolecular carbon–carbon approach is C(1) ··· C(8′) for both conformers, the corresponding carbon–hydrogen contacts are C(1) ··· H(8′) for the transoid and C(1) ··· H(2′) for the cisoid conformer. Similarly the penultimate contacts are C(2) ··· C(9′) and C(1) ··· H(2′) for the transoid conformer, compared with C(2) ··· C(2′) and C(1) ··· H(8′) for the cisoid conformer (Table 2). These intramolecular contact differences are associated with small aromatic ring bond length changes between the two conformers. While the lengths of the C(1)–C(8a) and the C(8)–C(8a) bonds are 1.433 and 1.413 Å, respectively, in the cisoid conformer,[1] there is a converse inequality in the lengths of the corresponding bonds of the transoid conformer (Figure 1).

TABLE 2

Non-bonded intramolecular atomic distances (Å). The primed atoms are related to corresponding non-primed atoms by the molecular C_2 symmetry

	trans	*cis* [a]		*trans*	*cis* [a]
C(1) ··· C(3′)	3.806	3.765	C(1) ··· H(2′)	2.676	2.594
C(1) ··· C(8′)	2.931	2.971	C(1) ··· H(8′)	2.569	2.631
C(1) ··· C(4a′)	3.827	3.818	C(2) ··· H(2′)	3.507	3.008
C(2) ··· C(2′)	3.420	3.108	C(2) ··· H(8′)	2.884	3.465
C(2) ··· C(8′)	3.393	3.891	C(8) ··· H(2′)	3.392	4.107
C(2) ··· C(8a′)	3.280	3.520	C(8) ··· H(8′)	3.867	2.992
C(8) ··· C(8′)	4.167	3.321	C(8a) ··· H(2′)	3.244	3.588
C(8) ··· C(8′)	3.738	3.331	C(8a) ··· H(8′)	3.230	2.813
C(8a) ··· C(8a′)	3.473	3.277	C(4a) ··· H(8′)	4.013	3.760
H(2) ··· H(2′)	3.701	2.950			
H(2) ··· H(8′)	3.067	3.825			
H(8) ··· H(8′)	3.806	2.908			

[a] From ref. 1.

The atoms of a given naphthalene ring system are not strictly coplanar in the active transoid structure (Table 3). The planes B and C refer to the individual benzene rings of a naphthalene residue (Figure 1) and plane A to the common mean plane of both rings in that residue (Table 3). The individual benzene rings and the naphthalene moiety are more puckered in the active transoid than the racemic cisoid conformer, as is shown by the root mean-square deviations from planarity recorded (Table 3) compared with the corresponding values of 90, 37, and 20 (Å/10^4) for the A, B, and C planes of the cisoid conformer.[1]

TABLE 3

The mean plane calculation for the individual benzenoid rings B and C (Figure 1) and for the naphthalene residue A. Deviations from the planes are shown in units of Å/10^4. Atoms not included in the planes are marked with an asterisk

Equations of the planes:

A $-0.4090X + 0.6973Y + 0.5886Z = 3.6314$
B $-0.4107X + 0.6879Y + 0.5984Z = 3.6814$
C $-0.4085X + 0.7064Y + 0.5781Z = 3.6034$

where $X = ax$, $Y = ay$, $Z = cz$, with $a = 7.2126$ and $c = 27.510$

	A	B	C
C(1)	−109	+22	−517 *
C(2)	−250	−87	−708 *
C(3)	+69	+88	−256 *
C(4)	+134	−23	−7 *
C(4a)	+155	−42	−73
C(5)	−69	−449 *	+39
C(6)	−261	−677 *	−98
C(7)	+11	−263 *	+42
C(8)	+224	+127 *	+69
C(8a)	+95	+43	−124
R.m.s. deviation	159	58	80

The Crystal Packing.—In the *R*-(−)-1,1′-binaphthyl crystal the molecules are packed around a 4_1 screw-axis along the *c* direction of the crystal (Figures 2 and 3). Relative to a given 4_1 screw-axis, the molecules form a series of coaxial right-handed helices of progressively larger radii. The initial two helices have radii, from the screw-axis to the mid-point of the C(1)–C(1′) bond of the molecule, of 3.23 and 4.03 Å with a rise per molecule along the screw-axis of 6.88 Å in each case. These two helices are related by a twofold screw axis (Figure 2). A given molecule is a member of two helices with the smaller radius, related to two individual 4_1 screw-axis and of two helices with the larger radius, related to two different 4_1 screw axis (Figure 2). The longer (L_1) and shorter (M_1) in-plane axis of one naphthalene moiety in the 1,1′-binaphthyl molecule lie at an angle of 42 and 73°, respectively, to the 4_1 screw-axis of the crystal, and the L_2 and M_2 axes of the second moiety are disposed at the corresponding supplementary angles, the two napththalene residues being related by the molecular twofold rotation axis perpendicular to the crystal 4_1 screw-axis (Figure 3).

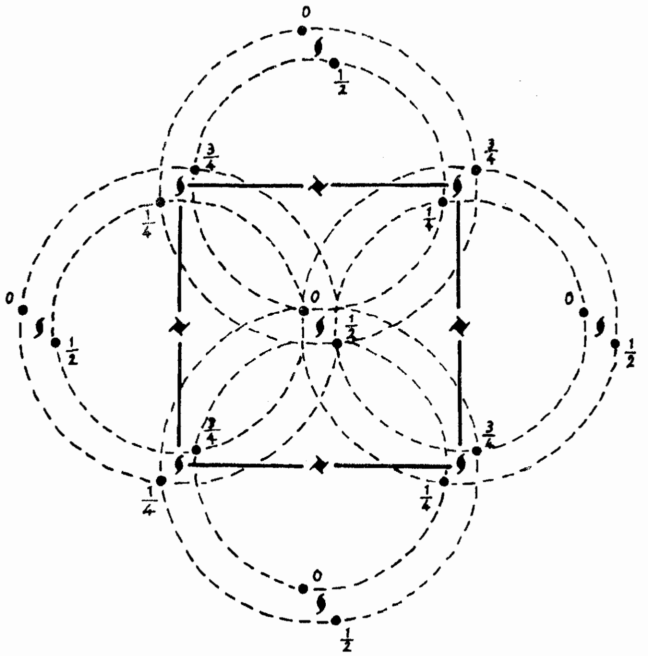

FIGURE 2 Schematic projection of the *R*-(−)-1,1′-binaphthyl crystal structure orthogonal to the *c*-axis. The circles centred on a given 4_1 screw axis symbol represent projections of the initial two helices around that axis

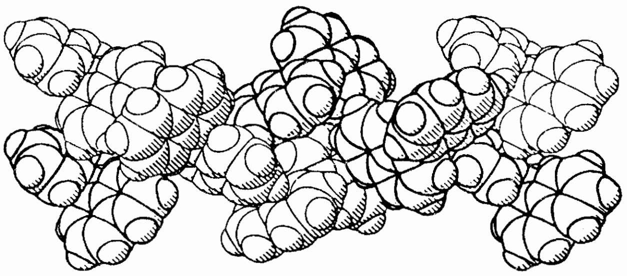

FIGURE 3 A spacing-filling projection of the *R*-(−)-1,1′-binaphthyl crystal structure on the *ac* plane. The two helices of molecules with the larger and the smaller helix radius relative to a given 4_1 screw-axis, and mutually related by a twofold screw-axis, are distinguished by a more and a less heavy outline

The resultant molecular packing in the active crystal is relatively loose, giving a crystal volume of 357.8 Å^3 per molecule, compared with 325.6 Å^3 per molecule for the more compact racemic crystal.[1] The closest intermolecular carbon–carbon and hydrogen–hydrogen contacts in the active crystal are 3.601 and 2.58 Å, respectively (Table 4), whereas intermolecular C···C and H···H distances as short as 3.45 and 2.46 Å, respectively, are observed in the racemic structure.[1] However, there are close C···H intermolecular interactions (2.845, 2.855 Å) in the active structure (Table 4), compared with a corresponding minimum distance of 2.90 Å in the racemic crystal.[1]

TABLE 4

Nearest-neighbour intermolecular distances (Å)

C(8a) ··· C(5)^{I}	3.601	H(5) ··· C(8)^{II}	2.845
C(4a) ··· C(5)^{I}	3.627	H(5) ··· C(4a)^{II}	2.855
C(4a) ··· C(6)^{I}	3.760	H(6) ··· C(4)^{II}	2.969
C(6) ··· C(4)^{II}	3.820	H(3) ··· C(8)^{III}	2.982
C(8) ··· C(5)^{I}	3.847	H(5) ··· C(7)^{II}	2.990
C(5) ··· C(5)^{I}	3.857		
		H(8) ··· H(6)^{IV}	2.576
		H(4) ··· H(3)^{V}	2.722
		H(8) ··· H(7)^{IV}	2.855

I $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} - z$
II $-\frac{1}{2} + x, -\frac{1}{2} - y, \frac{3}{4} - z$
III $-1 + y, x, \frac{1}{2} - z$
IV $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} - z$
V $y - 1, x - 1, \frac{1}{2} - z$

The reduced intermolecular C···H interactions in the racemic crystal are associated with an economic packing mode of homochiral layers of 1,1′-binaphthyl molecules in the *ab* plane of the crystal[1] (Figure 4).

Layers composed solely of the *R*-(−)-isomer alternating with layers made up of the *S*-(+)-enantiomer, and a given 1,1′-binaphthyl molecule is in close contact with four antipodal molecules, two in the upper and two in the lower contiguous layer. The C–H groups in the 3- and the 3′-position of a given 1,1′-binaphthyl molecule are directed towards the centre of the C′ and the C ring of the antipodal molecule in the upper and in the lower layer, respectively, while the C–H groups in the 7- and the 7′-position are directed towards the centre of the B′ and the B ring of the other antipodal molecules in the upper and the lower layer, respectively (Figure 4). As the π-electron charge density within each benzenoid ring is a minimum at the ring centre, this packing mode minimises the intermolecular non-bonding repulsions in respect of the 3-, 3′-, 7-, and the 7′-C–H groups. The insertions of these C–H groups into the ring-centre π-electron cavities form an interlocking network parallel to the *bc* plane of the crystal (Figure 4).

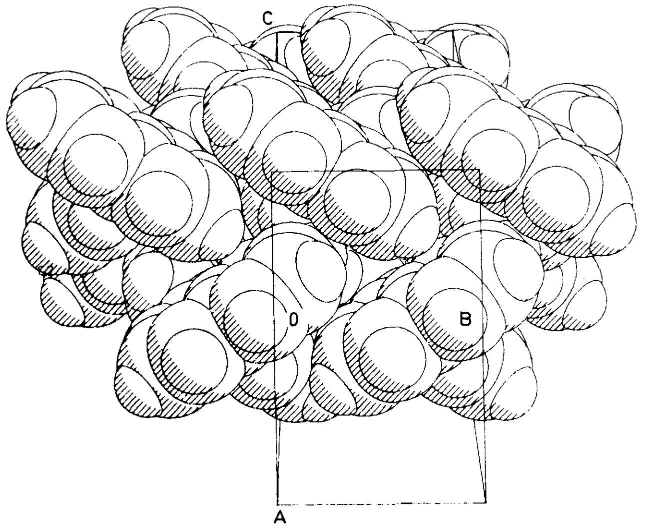

FIGURE 4 A spacing-filling projection of the racemic 1,1′-binaphthyl crystal structure, from ref. 1. The boxed outline refers to the unit cell with the origin 0 and the A, B, and C axes corresponding to the *a*, *b*, and *c* crystal axes, respectively

The set of homochiral layers in the *ab* plane of the racemic crystal form a herring-bone pattern, similar to that found in the crystals of the polyacene aromatic hydrocarbons[12] (Figure 4). The array is formed with the M axes of the naphthalene residues and the C(1)–C(1′) internuclear bonds nearly parallel to one another and to the *ab* crystal plane. The L axes of the naphthalene moieties lie at ±34° to the crystal *b*-axis along which the molecular twofold rotation axes are directed.

The racemic crystal is closely packed, with a density 9.4% larger than that of the active crystal. The density difference between an active and the corresponding racemic crystal is rarely so large.[5,13] In the minor class of racemates susceptible to self-resolution on crystallization, the active crystal is, as frequently as not, the more dense.[5] The racemic 1,1′-binaphthyl crystal belongs to one of the three space groups, $C2/c$, $P2_12_12$, and $Pbcn$, permitting a packing of maximum density for molecules with C_2 point group symmetry.[14] The closest-pack or maximum density criterion for a single enantiomer, of 1,1′-binaphthyl implies the space group, $P2_12_12$, which may represent an accessible high-pressure crystal-phase, detectable spectroscopically.

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