The Crystal and Molecular Structure of (*S*)-(+)- and Racemic 9,10-Dihydrodibenzo[*c,g*]phenanthrene

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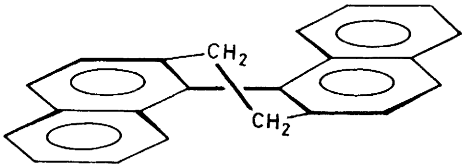
The molecular and crystal structures of the title bridged 1,1′-binaphthyls, (+)-BBN and (±)-BBN, have been determined from single-crystal *X*-ray data and refined by least-squares methods to *R* factors of 0.0597 and 0.0437, respectively. The unit-cell dimensions of (+)-BBN are, a = 8.1423(7), c = 39.216(4) Å, space group $P3_121$, with Z = 6, and of (±)-BBN, a = 20.018(2), c = 7.431(1) Å, space group $P4_2bc$ with Z = 8. The dihedral angle between the mean planes of the two naphthalene planes in a given molecule are similar (50 and 49°) in the two crystals, as are other intramolecular bond angles and the bond distances. The molecular packing modes in the two crystal lattices are compared.

THE present work reports *X*-ray diffraction determinations of the crystal and molecular structures of the racemate and of the (*S*)-(+)-isomer of 9,10-dihydrodibenzo[*c,g*]phenanthrene. The molecular structure of the (*S*)-(+)-isomer (1) is required for an analysis of the vibrational optical activity of the C–H stretching modes of the enantiomer, determined by i.r. c.d. measurements over the 2 800—3 100 cm^{-1} range,[1] and the comparison of the crystal structure of the enantiomer with that of the racemate concerns the general problem of the optical resolution of racemates.



(1)

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. Statistically some 70% of *ca.* 900 racemates are found to crystallize in the space groups, $P\bar{1}$, $P2_1/c$, and $C2/c$, all with inversion site symmetry.[2] A minor class of racemates, of which some 250 cases have been identified,[3] crystallize into a conglomerate of enantiomorphous active crystals, each containing a single enantiomer. In the minor class, chiral molecules with C_2 symmetry are represented statistically twice as frequently as molecules devoid of symmetry elements.[3]

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.[3,4] The comparison of the molecular packing modes in the lattices of corresponding active and racemic crystals is relevant to extensions of the entrainment method and other optical-resolution procedures based upon crystallization or, more generally, upon differences between the intermolecular interactions of optical antipodes. Improved optical-resolution procedures are significant in connection with the well established differential bioactivity of optical antipodes, and the widespread use of synthetic racemates in pharmacological and other biological applications.[5]

The class of chiral molecules with C_2 symmetry includes 1,1′-binaphthyl, which is dimorphic, crystallizing at ambient temperature [6] into a racemic form, m.p. 145°, and an optically active form, m.p. 158°. The racemic form is thermodynamically the more stable up to a transition temperature at 76°, and crystallization from the melt near to 150° affords a conglomerate of active crystals or, with appropriate seeding, crystals of a single enantiomer.[7] The molecule (1) is essentially a bridged 1,1′-binaphthyl (BBN) in which the 2,2′-ethano-bridge precludes the conformational lability found in the parent 1,1′-binaphthyl structure. The conformation of 1,1′-binaphthyl is *cisoid* in the racemic crystal,[8] but *transoid* in the crystal of the (*R*)-(—)-isomer,[9] the dihedral angle between the molecular planes of the two naphthalene nuclei in a given molecule being 68 and 103° in the racemic and in the active crystal, respectively. The large difference between the molecular conformation of 1,1′-binaphthyl in the racemic and in the active crystal is a limitation to the direct comparison of the packing modes of the molecule in the respective crystal lattices.

The conformational lability is reduced in the bridged 1,1′-binaphthyls, but not all these necessarily provide both a chiral and a racemic crystal. In the case of 1,1′-binaphthyl 2,2′-disulphide [10] the individual enantiomers have a higher melting point (262°) than that (214°) of the racemate, a property which is a necessary, but not sufficient, condition for self-resolution on crystallization.[3] At ambient temperature the recrystallization of racemic 1,1′-binaphthyl 2,2′-disulphide from chloroform afforded, in our hands, a conglomerate of the active crystals, so that only the structure of the chiral crystal lattice proved to be accessible,[11] although the racemate may be dimorphic,[12] like the parent compound, 1,1′-binaphthyl.[6] The 2,2′-ethano-bridged analogue (1), in contrast, has a racemate with a higher melting point (215—216°) than that (183°) of the individual enantiomers,[13] indicating that (±)-BBN forms a distinctive racemate lattice or a ' racemic compound ' in the traditional terminology.[14] With a conformationally constrained molecular structure, and the availability of both chiral and racemic crystal forms, BBN is an appropriate 1,1′-binaphthyl derivative for a comparison of the molecular packing modes in a chiral and the corresponding racemic crystal lattice. The well defined conformation of (*S*)-(+)-BBN in solution, in contrast to the corresponding lability and range of accessible conformers in the 2,2′-diamino-1,1′-binaphthyl enantiomers studied previously,[15] was the basis of a choice of (1) for an i.r. c.d. investigation of the vibrational optical activity of aromatic and aliphatic C–H stretching modes,[1] requiring in turn a quantitative molecular structure of (1).

EXPERIMENTAL

Samples of racemic and (*S*)-(+)-9,10-dihydrodibenzo-[*c,g*]phenanthrene (BBN), were kindly supplied by Dr. D. M. Hall,[13] and were recrystallized from diethyl ether and from ethyl methyl ketone, respectively. The transparent crystals, with a light yellow hue, employed for the intensity data collection had dimensions 0.25 × 0.27 × 0.18 mm for (+)-BBN and 0.20 × 0.24 × 0.39 mm for (±)-BBN. The unit-cell parameters for each crystal were determined from Weissenberg photographs and subsequently were refined on a diffractometer.

Crystal Data.—(i) (+)-BBN, $M = 280.3$. Trigonal, $a = 8.1423(7)$, $c = 39.216(4)$ Å, $U = 2\,251.6$ Å^3, $Z = 6$, $D_m = 1.24$, $D_c = 1.240$ g cm^{-3}, $F(000) = 888$, Cu-K_α radiation ($\lambda = 1.5418$ Å), μ(Cu-K_α) = 4.6 cm^{-1}, space group $P3_12\,1$.

(ii) (±)-BBN, $M = 280.3$. Tetragonal, $a = 20.018(2)$, $c = 7.431(1)$ Å, $U = 2\,977.9$ Å^3, $Z = 8$, $D_m = 1.25$, $D_c = 1.250$ g cm^{-3}, $F(000) = 1\,184$, Cu-K_α radiation ($\lambda = 1.5418$ Å), μ(Cu-K_α) = 4.6 cm^{-1}, space group $P4_2bc$.

Structure Determination.—Intensity data were collected on an Enraf–Nonius CAD-4 automatic diffractometer operated in the 2θ—θ scan mode up to $\theta = 70°$. The structures of both the (+)-BBN and the (±)-BBN crystal were solved by the direct method and both structures were refined by full-matrix least-squares procedures. In the case of the (+)-BBN crystal, some of the hydrogen atoms were not clearly apparent in the difference-Fourier map, and all the hydrogen atoms were located at their idealized positions. All hydrogen atoms were clearly evident in the difference-Fourier map of the (±)-BBN crystal, however, and their positional and thermal factors were refined. The atomic scattering factors for the carbon and for the hydrogen atoms were taken from refs. 16 and 17, respectively. The intensity data were not corrected for absorption and, for both crystals, each structure factor was assigned a unit weight. Calculations were carried out by means of the University of London CDC 7600 computer, employing the programs MULTAN 78 and SHELX 76.

The unique reflections were 2 567 out of 4 263 observed for the (+)-BBN crystal and 1 509 out of 2 814 observed for the (±)-BBN crystal. Equivalent reflections were averaged, and reflections with $|F_o| < 2\sigma$ (303 out of 2 567 for (+)-BBN and 84 out of 1 509 for (±)-BBN) were omitted from the refinement. The final *R* factors were 0.0597 for (+)-BBN and 0.0437 for (±)-BBN. The final atomic parameters with estimated standard deviations are listed for each of the two structures in Table 1. Observed and calculated structure amplitudes and thermal parameters of the atoms are tabulated in Supplementary Publication No. SUP 23041 (24 pp.).*

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*
(i) (+)-BBN			
Molecule (I)			
C(1)	4 960(10)	4 037(10)	94(2)
C(2)	4 023(12)	2 061(11)	91(2)
C(3)	4 841(13)	1 076(12)	244(2)
C(4)	6 551(13)	2 050(12)	413(2)
C(4a)	7 449(11)	4 042(12)	453(2)
C(5)	9 095(13)	5 029(13)	600(2)
C(6)	9 842(13)	6 911(14)	731(2)
C(7)	8 961(12)	7 897(12)	597(2)
C(8)	7 416(11)	7 002(11)	383(2)
C(8a)	6 620(10)	5 050(10)	299(2)
C(9)	2 028(12)	1 002(12)	−56(2)
Molecule (II)			
C(1)	738(10)	3 505(10)	1 528(2)
C(2)	971(11)	2 171(10)	1 347(2)
C(3)	2 230(12)	2 721(12)	1 069(2)
C(4)	3 296(11)	4 589(12)	978(2)
C(4a)	3 246(11)	6 012(11)	1 177(2)
C(5)	4 529(11)	7 977(12)	1 106(2)
C(6)	4 636(13)	9 338(13)	1 323(2)
C(7)	3 506(12)	8 821(12)	1 622(2)
C(8)	2 204(10)	6 942(11)	1 688(2)
C(8a)	2 008(10)	6 012(11)	1 464(2)
C(9)	−24(12)	150(11)	1 471(2)
(ii) (±)-BBN			
Molecule (III)			
C(1)	7 309(2)	177(2)	5 737(0)
C(2)	6 920(2)	−330(2)	5 009(8)
C(3)	6 303(2)	−501(2)	5 811(9)
C(4)	6 088(2)	−191(2)	7 344(9)
C(4a)	6 504(2)	275(2)	8 246(7)
C(5)	6 333(2)	544(2)	9 968(8)
C(6)	6 764(2)	922(2)	10 918(8)
C(7)	7 405(2)	1 060(2)	10 213(8)
C(8)	7 578(2)	836(2)	8 526(7)
C(8a)	7 137(2)	444(2)	7 473(7)
C(9)	7 188(2)	−717(2)	3 418(8)
C(1′)	7 928(2)	361(2)	4 760(7)
C(2′)	8 268(2)	−152(2)	3 879(7)
C(3′)	8 886(2)	−34(3)	3 057(8)
C(4′)	9 152(2)	593(3)	3 063(8)
C(4a′)	8 800(2)	1 141(2)	3 767(7)
C(5′)	9 040(2)	1 800(3)	3 578(8)
C(6′)	8 662(2)	2 337(2)	4 023(8)
C(7′)	8 001(2)	2 242(2)	4 743(8)
C(8′)	7 768(2)	1 602(2)	5 026(7)
C(8a′)	8 163(2)	1 032(2)	4 575(7)
C(9′)	7 935(3)	−820(2)	3 700(9)
H(3)	560(2)	−89(2)	523(6)
H(4)	559(2)	−31(2)	792(6)
H(5)	586(2)	42(2)	1 031(7)
H(6)	665(2)	113(2)	1 221(6)
H(7)	776(2)	134(2)	1 100(6)
H(8)	802(2)	91(2)	807(5)
H(91)	694(2)	−120(2)	317(8)
H(92)	715(2)	−41(2)	216(6)
H(3′)	916(3)	−44(3)	237(7)
H(4′)	960(3)	71(3)	270(9)
H(5′)	958(2)	189(2)	317(7)
H(6′)	883(2)	285(2)	405(7)
H(7′)	770(2)	266(2)	513(6)
H(8′)	730(2)	154(2)	554(5)
H(91′)	816(2)	−107(2)	261(7)
H(92′)	803(2)	−108(2)	479(6)

DISCUSSION

In the (+)-BBN structure there are two independent molecules, (I) and (II), each on a site of twofold symmetry. The unique molecule, (III), in the (±)-BBN

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* For details of Supplementary Publications see Notice to Authors No. 7, in *J. Chem. Soc. Perkin Trans. 2*, 1979, Index issue.

structure is located at a general position, but the molecular symmetry is C_2 in good approximation. The intramolecular bond lengths and angles of molecules (I) and (II) of the (+)-BBN structure and (III) of the (±)-BBN structure, based upon the atom numbering scheme of Figure 1, are compared in Table 2. The three molecular structure determinations give similar values for a given bond length or bond angle, and analogous molecular conformations.

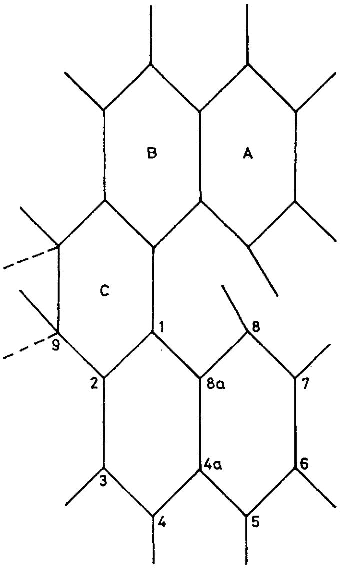

FIGURE 1 The atom-numbering scheme and ring-description of 9,10-dihydrodibenz[*c*,*g*]phenanthrene

The dihedral angle between the mean planes of the two naphthalene rings in a given molecule is 50° for each of the two molecular types in the optically active structure and 49° for the molecules of the more compact racemic structure (Table 3). The corresponding dihedral angle is larger (56°) in the structure[11] of (*S*)-(+)-1,1′-binaphthyl 2,2′-disulphide, due principally to the longer C–S (1.778 Å) and S–S (2.056 Å) bridging bonds relative to the C–C counterparts in the ethano-bridge of BBN (Table 2). The root-mean-square deviations of the naphthalene ring atoms from the mean plane of the aromatic nucleus are 0.080 and 0.086 Å for the two molecular types of (+)-BBN and 0.089 Å for (±)-BBN (Table 3), compared with 0.009 Å for racemic[8] and 0.016 Å for active[9] 1,1′-binaphthyl, or 0.087 Å for the bridged 2,2′-disulphide derivative.[11] The increase in the steric overcrowding of the 1,1′-binaphthyl molecule due to the 2,2′-bridging is not large, as is indicated by the theoretical potential energy curve as a function of the dihedral angle between the naphthalene planes in 1,1′-binaphthyl.[18] The theoretical curve is shallow, with a low inversion barrier to racemisation[18] (143 kJ mol^{-1}), the observed enthalpy of activation[19,20] (92, 90 kJ mol^{-1}) having an approximately comparable value.

The dihydro-ring C of BBN (Figure 1) has a skew-boat conformation with a dihedral angle between the 9–9′ bond and the 1–1′ bond of 46 and 45° for molecules (I)

TABLE 2

Intramolecular bond lengths (Å) and angles

(i) (+)-BBN

	Molecule (I)	Molecule (II)
C(1)–C(2)	1.394(6)	1.387(5)
C(2)–C(3)	1.407(7)	1.409(6)
C(3)–C(4)	1.380(7)	1.368(6)
C(4)–C(4a)	1.415(6)	1.415(6)
C(5)–C(4a)	1.424(6)	1.434(6)
C(5)–C(6)	1.365(7)	1.365(7)
C(6)–C(7)	1.417(8)	1.418(6)
C(7)–C(8)	1.379(6)	1.382(6)
C(8)–C(8a)	1.423(6)	1.420(5)
C(4a)–C(8a)	1.431(6)	1.427(5)
C(1)–C(8a)	1.428(5)	1.435(5)
C(1)–C(1′)	1.496(8)	1.507(8)
C(2)–C(9)	1.521(6)	1.505(6)
C(9)–C(9′)	1.511(10)	1.537(9)
C(2)–C(1)–C(8a)	119.0(4)	119.2(4)
C(1′)–C(1)–C(8a)	123.7(4)	123.9(4)
C(1′)–C(1)–C(2)	116.9(4)	116.9(4)
C(1)–C(2)–C(9)	118.1(4)	118.9(4)
C(1)–C(2)–C(3)	120.8(4)	120.6(4)
C(3)–C(2)–C(9)	120.9(4)	120.4(4)
C(2)–C(3)–C(4)	120.4(4)	120.8(4)
C(3)–C(4)–C(4a)	120.3(4)	120.3(4)
C(6)–C(5)–C(4a)	121.0(4)	120.0(4)
C(5)–C(6)–C(7)	119.5(4)	120.4(4)
C(6)–C(7)–C(8)	120.8(4)	120.6(4)
C(7)–C(8)–C(8a)	121.1(4)	120.9(4)
C(8)–C(8a)–C(4a)	117.4(4)	117.9(4)
C(8)–C(8a)–C(1)	123.2(4)	123.4(4)
C(1)–C(8a)–C(4a)	119.2(4)	118.6(4)
C(4)–C(4a)–C(5)	120.6(4)	120.2(4)
C(4)–C(4a)–C(8a)	119.4(4)	119.6(4)
C(5)–C(4a)–C(8a)	119.9(4)	120.0(4)

(ii) (±)-BBN

C(1)–C(2)	1.389(5)	C(1′)–C(2′)	1.394(5)
C(2)–C(3)	1.414(5)	C(2′)–C(3′)	1.400(6)
C(3)–C(4)	1.366(6)	C(3′)–C(4′)	1.364(7)
C(4)–C(4a)	1.418(6)	C(4′)–C(4a′)	1.405(6)
C(5)–C(4a)	1.430(6)	C(5′)–C(4′a)	1.411(6)
C(5)–C(6)	1.348(6)	C(5′)–C(6′)	1.356(7)
C(6)–C(7)	1.413(6)	C(6′)–C(7′)	1.440(6)
C(7)–C(8)	1.376(5)	C(7′)–C(8′)	1.380(5)
C(8)–C(8a)	1.417(5)	C(8′)–C(8a′)	1.427(5)
C(4a)–C(8a)	1.432(5)	C(4a′)–C(8a′)	1.426(4)
C(1)–C(8a)	1.439(5)	C(1′)–C(8a′)	1.432(4)
C(2)–C(9)	1.511(6)	C(2′)–C(9′)	1.499(6)
C(1)–C(1′)	1.482(4)	C(9)–C(9′)	1.524(6)
C(2)–C(1)–C(8a)	119.1(3)	C(2′)–C(1′)–C(8a′)	119.1(3)
C(1′)–C(1)–C(8a)	123.2(3)	C(1)–C(1′)–C(8a′)	123.7(3)
C(1′)–C(1)–C(2)	117.3(3)	C(1)–C(1′)–C(2′)	117.1(3)
C(1)–C(2)–C(9)	118.7(3)	C(1′)–C(2′)–C(9′)	118.8(4)
C(1)–C(2)–C(3)	120.1(4)	C(1′)–C(2′)–C(3′)	120.8(4)
C(3)–C(2)–C(9)	121.1(4)	C(3′)–C(2′)–C(9′)	120.2(4)
C(2)–C(3)–C(4)	121.2(4)	C(2′)–C(3′)–C(4′)	119.9(4)
C(3)–C(4)–C(4a)	120.5(4)	C(3′)–C(4′)–C(4a′)	121.6(4)
C(6)–C(5)–C(4a)	121.9(4)	C(6′)–C(5′)–C(4a′)	121.8(4)
C(5)–C(6)–C(7)	119.8(4)	C(5′)–C(6′)–C(7′)	119.9(4)
C(6)–C(7)–C(8)	120.2(4)	C(6′)–C(7′)–C(8′)	119.4(4)
C(7)–C(8)–C(8a)	121.8(4)	C(7′)–C(8′)–C(8a′)	121.2(4)
C(8)–C(8a)–C(4a)	117.5(3)	C(8′)–C(8a′)–C(4a′)	118.2(3)
C(8)–C(8a)–C(1)	123.5(3)	C(8′)–C(8a′)–C(1′)	123.0(3)
C(1)–C(8a)–C(4a)	119.0(3)	C(1′)–C(8a′)–C(4a′)	118.5(3)
C(4)–C(4a)–C(5)	122.1(4)	C(4′)–C(4a′)–C(5′)	121.4(4)
C(4)–C(4a)–C(8a)	119.0(4)	C(4′)–C(4a′)–C(8a′)	119.1(4)
C(5)–C(4a)–C(8a)	118.8(4)	C(5′)–C(4a′)–C(8a′)	119.3(4)
C(3)–H(3)	1.08(3)	C(3′)–H(3′)	1.11(5)
C(4)–H(4)	1.11(4)	C(4′)–H(4′)	0.96(6)
C(5)–H(5)	1.02(4)	C(5′)–H(5′)	1.14(4)
C(6)–H(6)	1.07(4)	C(6′)–H(6′)	1.07(5)
C(7)–H(7)	1.08(3)	C(7′)–H(7′)	1.07(5)
C(8)–H(8)	0.96(3)	C(8′)–H(8′)	1.03(3)
C(9)–H(91)	1.11(4)	C(9′)–H(91′)	1.05(5)
C(9)–H(92)	1.12(4)	C(9′)–H(92′)	0.98(5)

TABLE 3

The mean plane calculation for the individual benzenoid rings (A) and (B) (Figure 1) and for the naphthalene residue (N). Deviations from the planes are shown in units of 10^{-3} Å. Atoms not included in the planes are marked with an asterisk. x, y, and z in the equations are fractional co-ordinates

(i) (*S*)-(+)-BBN

Molecule (I)

Equation of the planes

(N) $-4.500x + 1.065y + 32.011z = -1.389$
(B) $-4.438x + 1.587y + 32.690z = -1.195$
(A) $-4.514x + 0.585y + 31.288z = -1.736$

	(N)	(B)	(A)
C(1)	−112	−59	27 *
C(2)	90	34	325 *
C(3)	106	15	377 *
C(4)	−19	−37	191 *
C(4a)	−82	11	28
C(5)	−56	114 *	−10
C(6)	36	313 *	−15
C(7)	108	423 *	21
C(8)	23	267 *	−3
C(8a)	−95	36	−21
R.m.s. deviation	80	36	18

Molecule (II)

Equation of the planes

(N) $6.695x - 3.427y + 22.315z = 2.828$
(B) $6.435x - 2.820y + 23.928z = 3.205$
(A) $6.898x - 3.932y + 20.663z = 2.279$

	(N)	(B)	(A)
C(1)	−125	−62	9 *
C(2)	84	31	320 *
C(3)	118	21	398 *
C(4)	−11	−38	211 *
C(5)	−61	106 *	−6
C(6)	28	310 *	−19
C(7)	116	445 *	22
C(8)	35	295 *	0
C(8a)	−96	44	−25
C(4a)	−88	5	28
R.m.s. deviation	86	38	20

Dihedral angles between planes

Molecule (I)				Molecule (II)			
	(N)	(B)	(A)		(N)	(B)	(A)
(B)	4.6			(B)	4.9		
(A)	4.1	8.7		(A)	4.3	9.2	
(N′) *	49.9	45.5	53.8	(N′)	49.8	45.2	53.8
(B′)	45.5	41.0	49.4	(B′)	45.2	41.0	49.3
(A′)	53.8	49.4	57.7	(A′)	53.8	49.3	57.8

* A primed plane is related to the corresponding unprimed plane by a two-fold rotation.

(ii) (±)-BBN

Equation of planes

(N) $-8.368x + 15.642y - 3.442z = -7.940$
(B) $-9.178x + 14.532y - 3.809z = -8.704$
(A) $-7.533x + 16.528y - 3.123z = -6.995$

	(N)	(B)	(A)
C(1)	126	68	−11 *
C(2)	−91	−34	−328 *
C(3)	−118	−22	−396 *
C(4)	19	42	−201 *
C(4a)	89	−6	−26
C(5)	61	−114 *	10
C(6)	−36	−322 *	13
C(7)	−114	−442 *	−21
C(8)	−28	−283 *	5
C(8a)	90	−47	18
R.m.s. deviation	86	41	17

TABLE 3 (*continued*)

Equation of the planes

(N′) $8.640x - 1.566y + 6.678z = 9.847$
(B′) $9.357x - 3.088y + 6.468z = 10.323$
(A′) $9.897x - 0.2183y + 6.828z = 9.527$

	(N′)	(B′)	(A′)
C(1′)	125	62	−24 *
C(2′)	−89	−31	−346 *
C(3′)	−123	−21	−422 *
C(4′)	13	38	−221 *
C(4a′)	93	−48	−30
C(5′)	71	−106 *	16
C(6′)	−42	−338 *	9
C(7′)	−118	−461 *	−19
C(8′)	−30	−298 *	4
C(8a′)	99	−45	21
R.m.s. deviation	89	43	19

Dihedral angles between planes

	(N)	(B)	(A)	(N′)	(B′)
(B)	4.8				
(A)	4.3	9.1			
(N′)	48.9	44.3	52.8		
(B′)	44.0	39.4	48.0	5.0	
(A′)	53.2	48.7	57.1	4.5	9.6

and (II) of the (+)-BBN structure and 44° for the unique molecule (III) of the (±)-BBN structure. The internuclear 1–1′ bond has a length, 1.496(8), 1.507(8), and 1.482(4) Å for the BBN molecules (I)—(III), respectively, intermediate between the corresponding values for racemic[8] (1.475 Å) and active[9] (1.511 Å) 1,1′-binaphthyl.

The intramolecular steric overcrowding in the BBN molecule is the more pronounced between the aliphatic bridge and aromatic carbon atoms, and between the respective hydrogen atoms bonded to those carbon atoms, than between the aromatic carbon atoms themselves, or the hydrogen atoms bonded to them (Table 4). The average C(8) · · · C(8′) separation (3.072 Å) is larger than the corresponding distance (3.0 Å) found[21] in the parent aromatic hydrocarbon, dibenzo[*c,g*]phenanthrene ([5]-helicene), and is comparable to the mean C(1) · · · C(8′) separation (3.048 Å). Across the dihydro-ring C, however, the C(1) · · · C(9) separation is 2.800 Å (Table 4). The smallest hydrogen–hydrogen intramolecular distances are those between the atoms of the adjacent CH_2 groups of the ethano-bridge, and between a hydrogen atom of each of those groups and the nearest neighbour hydrogen bonded to an aromatic nucleus (Table 4). The non-bonded intramolecular carbon–hydrogen contacts are closer, with the averaged separations of 2.619 and 2.678 Å for H(8) · · · C(8a′) and H(8) · · · C(8′), respectively (Table 4).

Crystal Structure.—(i) (+)-*BBN*. The projection of the (+)-BBN structure along the (110) direction (Figure 2) shows that the six molecules in a unit cell are made up of three molecules (I) interleaved with three molecules (II) around the crystal 3_1 screw-axis in a period of 39.216 Å. Each molecular C_2 axis is orthogonal to the crystal *c*-axis, and the screw translation along that axis, from molecule (I) to (II), involves a rotation of the molecule about its C_2 axis of ±74.4° and a small displacement in the (110) direction. The internuclear 1–1′ bonds of

TABLE 4

Non-bonded intramolecular atomic distances (Å)

(i) (+)-BBN

	Molecule (I)	Molecule (II)
C(3) · · · C(1′)	3.776	3.779
C(8) · · · C(1′)	3.043	3.060
C(9) · · · C(1′)	2.795	2.801
C(2) · · · C(2′)	2.857	2.855
C(8a) · · · C(2′)	3.703	3.711
C(9) · · · C(3′)	3.653	3.673
C(8) · · · C(8′)	3.061	3.113
C(8a) · · · C(8′)	3.218	3.248
C(8a) · · · C(8a′)	3.223	3.246
H(8) · · · C(1′)	2.706	2.728
H(91) · · · C(1′)	2.995	2.931
H(91) · · · C(2′)	2.715	2.662
H(92) · · · C(3)	2.626	2.591
H(8) · · · C(8′)	2.635	2.707
H(8) · · · C(8a′)	2.592	2.636
H(3) · · · C(9)	2.755	2.733
H(8) · · · H(8′)	2.62	2.70
H(92) · · · H(3)	2.41	2.36
H(92) · · · H(91′)	2.58	2.60
H(92) · · · H(92′)	2.50	2.64

(ii) (±)-BBN

C(1) · · · C(3′)	3.756	C(3) · · · C(1′)	3.764
C(1) · · · C(8′)	3.043	C(8) · · · C(1′)	3.038
C(1) · · · C(9′)	2.800	C(1′) · · · C(9)	2.799
C(2) · · · C(2′)	2.847	C(8) · · · C(8′)	3.043
C(2) · · · C(8a′)	3.706	C(8a) · · · C(2′)	3.699
C(8) · · · C(8a′)	3.185	C(8′) · · · C(8a)	3.205
H(8′) · · · C(1)	2.728	H(8) · · · C(1′)	2.703
H(92) · · · C(1)	2.926	H(92) · · · C(1′)	2.923
H(92′) · · · C(2)	2.686	H(92′) · · · C(1′)	2.855
H(91) · · · C(3)	2.728	H(91′) · · · C(3′)	2.554
H(8′) · · · C(8)	2.685	H(8) · · · C(8′)	2.699
H(8′) · · · C(8a)	2.636	H(8) · · · C(8a′)	2.624
H(3) · · · C(9)	2.758	H(3′) · · · C(9′)	2.752
H(8′) · · · H(8)	2.69	H(91′) · · H(91)	2.50
H(91) · · · H(3)	2.50	H(91′) · · · H(3′)	2.38
H(92′) · · · H(91)	2.52	H(91′) · · · H(92)	2.43

molecules (I) and (II) are nearly orthogonal, lying at an angle of 93.2° to one another.

In the (+)-BBN lattice, the molecules (I) form layers perpendicular to the crystal *c*-axis, sandwiching analogous layers made up of molecule (II). In a given layer, the C_2 axes of all the molecules, whether (I) or (II), are parallel to one another with a translation of 8.1423 Å between neighbours. The packing of molecules with collinear C_2 axes in a given layer is efficient, with the ethano-bridging group of one molecule keyed into the dihedral volume between the two naphthalene rings of its immediate neighbour (Figure 2).

The closest intermolecular contacts in the (+)-BBN crystal refer to this particular packing feature (SUP 23041). The bridging 9-CH_2 group of one molecule and the aromatic 7-CH group of its neighbour with a collinear C_2 molecular axis in a given layer have a C · · · C and a H · · · H separation of 3.589 and 2.335 Å, respectively, averaged for the two layer types. Between adjacent layers, the intermolecular C · · · C and H · · · H separations of molecule (I) from (II) are larger, but the closest intermolecular carbon–hydrogen contact (2.647 Å) refers to the interval between C(8a) and H(4) of molecules (I) and (II) in contiguous layers (SUP 23041).

The packing of each molecular type in the (+)-BBN lattice is individually analogous to that of (+)-1,1′-binaphthyl 2,2′-disulphide, where the bridging S–S bond is nearly parallel to the *b*-axis of the crystal, with a molecular translation of 10.32 Å along the *c*-axis.[11] The ethano-bridging 9–9′ bond of molecule (II) is almost parallel to the *c*-axis of the (+)-BBN crystal, lying at an angle of 1.3°, and the corresponding 9–9′ bonds of the molecules (I) in a given layer are parallel to one another, each making an angle of 73.1° with the crystal *c*-axis. The molecular translation of (II) along the *b*-axis and of (I) along the (110) direction in the (+)-BBN lattice, 8.1423 Å in each case, is smaller than the corresponding translation in the disulphide-bridged lattice due to the compact layer structure which limits, however, the mutual interpenetration of the contiguous layers. In the lattice of (+)-1,1′-binaphthyl 2,2′-disulphide, which crystallizes in the space group, $P2_1$, no layer structure is observed perpendicular to the crystal *b*-axis, and the molecules related by the 2_1 screw axis are closely interleaved. The S–S bonds of the disulphide-bridged molecules translationally equivalent along the crystal *b*-axis are in van der Waals contact end-to-end, resulting in a *b*-axis interval of 5.755 Å between adjacent molecules. In contrast the mean rise per molecule in the (+)-BBN structure along the 3_1 screw-axis is 6.536 Å, due to the restricted interleaving of adjacent layers.

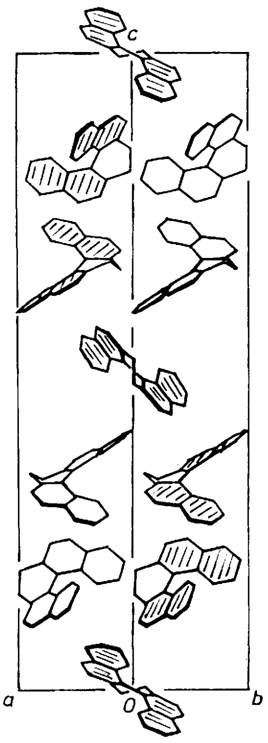

FIGURE 2 The projection of the (+)-BBN structure along the (110) direction. The molecules related by a 3_1 screw-axis are shaded

(ii) (±)-*BBN*. The projection of the (±)-BBN structure perpendicular to the crystal *c*-axis (Figure 3) shows that the eight molecules in a unit cell are made up of four (*S*)-(+)-BBN molecules, forming a turn of the 4_2 screw-axis with a repeat period of 7.431 Å, and four (*R*)-(−)-BBN molecules, related to their antipodes by a glide plane, forming an analogous 4_2 repeat unit. Molecules of the same chirality stack in a set of four homochiral columns around a 4_2 screw-axis along the crystal *c*-axis. Each set of homochiral columns of (*S*)-(+)-BBN molecules is surrounded by four adjacent and parallel sets of homochiral columns of (*R*)-(−)-BBN, and *vice versa*.

Perpendicular to the crystal *c*-axis, the four homochiral molecules of a given 4_2 repeat unit form two layers, the two molecules in a particular layer being related by the crystal C_2 [≡$(4_2)^2$] axes (Figure 3). The layers include corresponding antipodal molecules of adjacent homochiral columns and they extend infinitely. All the molecules in a given layer, whether (*S*)-(+)-BBN or (*R*)-(−)-BBN, have their molecular C_2 axes nearly parallel to a crystal plane, the *ac*-plane for one layer and the *bc*-plane for each neighbouring layer. Each molecular C_2 axis is orientated at an angle of 58.9° to the crystal *c*-axis, such that the array of molecular C_2 axes in the set of four homochiral columns passing through the (*S*)-(+)-BBN 4_2 repeat units forms a right-handed helix, whereas the corresponding array for a set of four (*R*)-(−)-BBN homochiral columns represents a left-handed helix (Figure 3).

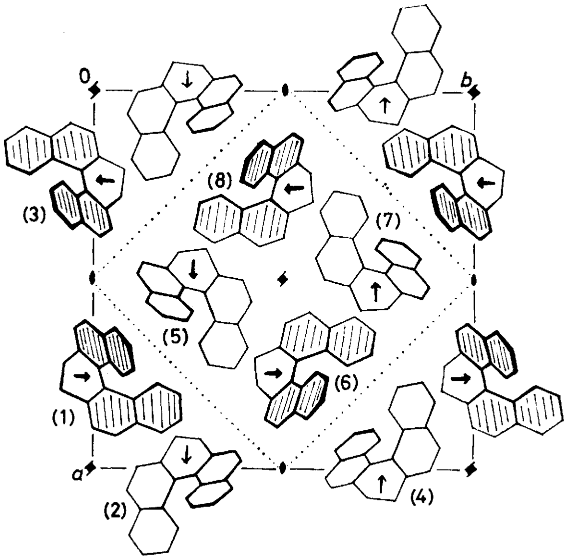

FIGURE 3 The projection of the (±)-BBN structure perpendicular to the crystal *c*-axis. Molecules (1)—(4) are (*R*)-(−)-BBN and (5)—(8) are (*S*)-(+)-BBN. The shaded molecules form one layer of the structure, with an adjacent layer of unshaded molecules below or above. The arrows represent the molecular C_2 axes with the arrowheads directed upwards

The mean molecular planes of the molecules making up each of the homochiral columns along the crystal *c*-axis, while parallel to one another, are tilted with respect to the *c*-axis, on account of the steric requirements of the relatively bulky CH_2 groups of the ethano-bridge in BBN. The CH_2 groups of the bridge in each BBN molecule partly occupy the dihedral void between the naphthalene rings of a homochiral molecule related by the 4_2 symmetry operation. In addition, the dihedral void is partly occupied by a naphthalene ring of an adjacent antipodal BBN molecule related by a glide plane. Thus the dihedral space of the BBN molecule, (*R*)-(−)-(1), is partly occupied by the ethano-bridge of (*R*)-(−)-(2) in the layer above, and by aromatic C–H groups of (*S*)-(+)-(5) in the layer below (Figure 3). The smallest intermolecular separations in the (±)-BBN structure refer to these and the analogous interlayer contacts, involving C · · · C and H · · · H separations comparable to the close intralayer contacts in the (+)-BBN structure (SUP 23041).

Structure Comparison.—The packing modes of maximum density for a molecule with C_2 symmetry require a crystal belonging to the space group $P2_12_12$ for the optically active structure and to either $C2/c$ or $Pbcn$ for the racemic structure.[22] The crystals of neither (+)-BBN nor (±)-BBN conform to the maximum-density criterion for the molecular packing modes in a crystal, each of the structures having the higher symmetry of a trigonal and a tetragonal crystal system, respectively. The racemic structure is the more compact, although the density of the (±)-BBN crystal is only 0.8% larger than that of the corresponding active crystal, whereas in the case of 1,1′-binaphthyl the racemic is 9.4% more dense than the active crystal.[9]

The BBN molecule has the overall morphology of a helical segment, and molecular models indicate that there are two efficient packing modes of homochiral helical segments with C_2 symmetry. The first packing mode entails intermolecular contact with collinear molecular C_2 axes, with a form exemplified by the layer structure of the (+)-BBN lattice, and the second consists in the homochiral stacking of the molecules with the mean molecular planes parallel to one another, as is found in the homochiral column structure of the (±)-BBN crystal. The two economic packing modes are not mutually compatible, since the insertion of the ethano-bridging group of one molecule into the dihedral void between the naphthalene rings of a second molecule with a collinear C_2 axis precludes the close stacking of a third with a mean molecular plane parallel to the corresponding plane of either of the other two molecules.

The packing of two antipodal BBN molecules, from molecular models, is not efficient with collinear molecular C_2 axes or with parallel mean molecular planes. In the (±)-BBN lattice nearest neighbour antipodal molecules are located in contiguous layers with the respective molecular C_2 axes parallel to orthogonal crystal planes. The orthogonal disposition allows into the dihedral volume of BBN the entry of aromatic C–H groups of a heterochiral molecule as well as the aliphatic CH_2 groups of a homochiral molecule, exemplied by the closest intermolecular contacts between (*S*)-(+)-(5) and (*R*)-(−)-(1), and between the latter and (*R*)-(−)-(2), in successive layers (Figure 3, SUP 23041). Both these features, and the homochiral stacking along the crystal *c*-axis, are conducive to a compact structure, although they do not lead to a packing mode of maximum density for a racemate of molecules with C_2 point symmetry.

The adoption of the homochiral column stacking in the racemic but not in the optically active crystal of BBN has an analogy in the corresponding packing modes of the racemic and the Δ-(−)-tris(pentane-2,4-dionato)-chromium(III) crystal.[23] Tris-chelate complexes with D_3 point symmetry stack efficiently in homochiral columns with the molecular C_3 axis parallel, or at a small angle, to the column axis, whereas the packing of such molecules along the direction of a molecular C_2 axis, retaining parallel C_3 axes, is economic only if neighbouring molecules are antipodal isomers. The efficient packing of two homochiral D_3 molecules with collinear C_2 molecular axes involves the mutual rotation of the principal molecular axis to the tetrahedral angle or its supplement. The racemic $[Cr(pd)_3]$ crystal is made up of homochiral columns, with adjacent and parallel columns composed of antipodal isomers, but such columns are absent in the corresponding chiral lattice. The structure of the Δ-(−)-$[Cr(pd)_3]$ crystal, which contains two independent molecules in the asymmetric unit, is characterised by four relationships between the principal molecular axes, three being the supplement of the tetrahedral angle and the fourth a nearly parallel alignment.[23]

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