Crystal and Molecular Structure of [5]Helicene: Crystal Packing Modes

By **Reiko Kuroda**,* Department of Chemistry, King's College London, Strand, London WC2R 2LS

The crystal and molecular structure of two crystal habits of [5]helicene, forms A and B, have been determined and their respective crystal packing modes are compared, together with those of other members of the helicene series. Form A crystallizes from n-pentane in the space group $P2_1/c$ with a = 5.8150(7), b = 14.178(1), c = 17.498(1) Å, β = 94.41(1)°, Z = 4, while form B from ethanol solution belongs to the space group $A2/a$ with a = 26.013(2), b = 8.898(1), c = 19.494(2) Å, β = 103.94(1)°, Z = 12.

THE determination by X-ray diffraction methods of the crystal and molecular structure of [5]helicene in two racemic structure modifications is reported in the present study. The objects of the work described are two-fold. First, the intramolecular contacts in [5]helicene are large enough to allow the compound to become optically active, but not too severe, the $\tau_{\frac{1}{2}}$ of racemization being *ca.* 14 h at ambient temperature.[1] The racemization of helicenes of higher number is prevented, with only [6]-helicene racemizing at the m.p. temperature.[2] A comparison of the molecular structure of [5]helicene with the corresponding structures of the other members of the series is, therefore, of interest. Secondly, while almost all other helicenes crystallize in enantiomorphous space groups and are spontaneously resolved on crystallization, [5]helicene crystallizes in at least two racemic crystal forms. The determination of the lattice structure of both of these forms is expected to throw light on the factors governing solid-state chiral discrimination, particularly those leading to the spontaneous resolution of racemates on crystallization.

The present work continues our previous studies [3,4] of the crystal and molecular structures of enantiomers and their corresponding racemates, 1,1'-binaphthyl (BN), which crystallizes [5] into a conglomerate of active crystals above 76 °C, and the ethano-bridged 1,1'-binaphthyl (BBN), or dihydro[5]helicene, which crystallizes as a racemate.[6]

Both of the racemic forms of [5]helicene are monoclinic. One crystallizes in the space group of $P2_1/c$ with $Z = 4$ (form A) for which only the crystal data were reported by Harnik *et al.*[7] in 1951. The other form (form B) belongs to the space group $A2/a$ with $Z = 12$, and the determination of this complicated structure was attempted [8] as early as 1954, although the work was understandably incomplete and partially incorrect. In the present work, the crystal and molecular structures of both forms have been determined. It would be of interest to compare these structures with that of the corresponding chiral crystal, the optical resolution having been reported by the methods of Newman and Lednitzer.[1] The crystal packing modes of the other members of the helicene group, not discussed previously, are also compared.

* *Present address:* Department of Biophysics, King's College London, 26—29 Drury Lane, London WC2B 5RL.

EXPERIMENTAL

Samples of racemic [5]helicene were kindly supplied by Dr. A. Collet. Recrystallization from n-pentane produced crystals of form A and from ethanol form B. Crystals of form B have an orange hue, while form A has a normal, very pale yellow colour. The crystals employed for the data collection had dimensions $0.25 \times 0.38 \times 0.23$ mm and $0.08 \times 0.33 \times 0.25$ mm for the A and B forms, respectively. The unit-cell parameters for each of the crystals were determined from Weissenberg photographs and subsequently refined on a diffractometer.

Crystal Data.—(i) Form A: $C_{22}H_{14}$, $M = 278.35$, monoclinic, $a = 5.8150(7)$, $b = 14.178(1)$, $c = 17.498(2)$ Å, $\beta = 94.41(1)°$, $U = 1438.3$ Å^3, $Z = 4$, $D_m = 1.28$, $D_c = 1.285$ g cm^{-3}, $F(000) = 584$, Cu-K_α radiation $(\lambda = 1.5418$ Å$)$, μ(Cu-K_α) = 4.8 cm^{-1}, space group $P2_1/c$.

(ii) Form B: $C_{22}H_{14}$, $M = 278.35$, monoclinic, $a = 26.013(2)$, $b = 8.898(1)$, $c = 14.494(2)$ Å, $\beta = 103.94(1)°$, $U = 4379.0$ Å^3, $Z = 12$, $D_m = 1.27$, $D_c = 1.266$ g cm^{-3}, $F(000) = 1$ 752, Cu-K_α radiation $(\lambda = 1.5418$ Å$)$, μ(Cu-K_α) = 4.7 cm^{-1}, space group $A2/a$. Space group $A2/a$, rather than the standard $C2/c$, was adopted for the form B in order to facilitate the comparison of the structure with that of the previous determination.[8]

Structure Determination.—Intensity data were collected on an Enraf–Nonius CAD-4 automatic diffractometer operated in the 2θ–θ scan mode up to $\theta = 65°$ for each of the crystals. The structures of both the A and B forms were solved by the direct method employing MULTAN 78 and were refined by full-matrix least-squares procedures using SHELX 76.

In the case of form B, the density and molecular weight together with the unit-cell volume indicated that there are twelve molecules in the unit cell. This corresponds to two independent molecules, one of which, molecule (I), is in a general position and the other, molecule (II), is in a special position. All the carbon atoms of molecule (I), together with some extra peaks and a few peaks probably corresponding to the carbon atoms of the second molecule, were revealed in the first E map. However, the structure could not be refined by the routine application of full-matrix least-squares procedures. The R factor stayed at 0.53 and the subsequent difference map showed no sensible peaks. Location of the molecules in completely different positions in the unit-cell, as had appeared in the E map of the other sets, or slightly different initial positioning for the least-squares refinements also failed, leading to convergence to similar high R values. The least-squares refinements with a damping factor for the parameter shift or with a cut-off of intensity data based on sin θ were also unsuccessful. A similar problem of refinement of the structure was en-

countered with [7]helicene.[9] The full-matrix least-squares refinement with a constraint in the molecular geometry, on the other hand, brought the R factor down to 0.35 and some of the missing carbon atoms of molecule (II) were revealed. A series of full-matrix least-squares refinements and difference Fourier maps gradually located all the carbon atoms. All the hydrogen atoms were revealed in difference Fourier maps, after employing anisotropic temperature factors for the carbon atoms. Isotropic temperature as well as positional parameters of the hydrogen atoms were refined. The geometric constraints were removed at the last stage. The final R factor was 0.068. Out of 2 720 unique reflections, 596 with $|F_o| < 3\sigma(F_o)$ were suppressed from the refinement. The biggest difference between the initial co-ordinates of molecule (I) as shown in the E map and the ones refined was 0.16 Å and, on average, the shift was only 0.03 and 0.02 Å along the a and c directions, respectively.

The structure determination of form A, on the other hand, was straightforward. Anisotropic and isotropic temperature factors were employed for the carbon and the hydrogen atoms, respectively. Out of 2 998 unique reflections observed, 2 537 with $|F_o| \geqslant 3\sigma(F_o)$ were employed for the refinement. The final R value was 0.060. All the computations were carried out on the CDC 7600, University of London. The atomic scattering factors for the carbon and for the hydrogen atoms were taken from refs. 10 and 11,

TABLE 1

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

(i) Crystal A, molecule (III)

	x	y	z
C(1)	2 071(3)	5 210(1)	1 213(1)
C(2)	2 346(4)	5 726(2)	563(1)
C(3)	4 417(4)	6 196(2)	470(2)
C(4)	6 104(4)	6 189(2)	1 050(2)
C(4a)	5 839(3)	5 695(1)	1 737(1)
C(5)	7 487(4)	5 806(2)	2 375(2)
C(6)	7 040(5)	5 462(2)	3 058(2)
C(6a)	5 064(4)	4 898(2)	3 161(1)
C(7)	4 545(7)	4 621(2)	3 904(2)
C(8)	2 639(7)	4 126(2)	4 015(2)
C(8a)	1 229(5)	3 745(2)	3 381(1)
C(9)	−737(6)	3 185(2)	3 500(2)
C(10)	−1 986(6)	2 783(2)	2 920(2)
C(10a)	−1 214(4)	2 793(2)	2 158(2)
C(11)	−2 250(5)	2 222(2)	1 562(2)
C(12)	−1 296(5)	2 123(2)	887(2)
C(13)	777(5)	2 577(2)	768(2)
C(14)	1 778(4)	3 158(1)	1 324(1)
C(14a)	780(3)	3 321(1)	2 021(1)
C(14b)	1 848(4)	3 920(1)	2 624(1)
C(14c)	3 575(4)	4 630(1)	2 520(1)
C(14d)	3 831(3)	5 145(1)	1 812(1)
H(1)	61(4)	493(1)	128(1)
H(2)	104(4)	579(2)	16(1)
H(3)	455(5)	658(2)	−3(2)
H(4)	761(5)	654(2)	102(1)
H(5)	898(5)	627(2)	229(2)
H(6)	803(5)	557(2)	350(2)
H(7)	566(5)	481(2)	437(2)
H(8)	215(5)	397(2)	451(2)
H(9)	−114(5)	316(2)	407(2)
H(10)	−336(5)	244(2)	294(2)
H(11)	−368(5)	190(2)	169(2)
H(12)	−199(5)	169(2)	48(2)
H(13)	158(4)	245(2)	28(2)
H(14)	322(4)	344(2)	126(1)

TABLE 1 (continued)

(ii) Crystal B, molecule (I)

	x	y	z
C(1)	−345(2)	1 375(5)	4 004(2)
C(2)	−178(2)	2 586(6)	4 425(3)
C(3)	348(3)	2 739(8)	4 801(3)
C(4)	690(2)	1 625(8)	4 769(3)
C(4a)	538(2)	340(6)	4 349(2)
C(5)	885(2)	−902(9)	4 372(3)
C(6)	711(2)	−2 207(8)	4 080(3)
C(6a)	181(2)	−2 382(6)	3 666(3)
C(7)	−17(3)	−3 821(7)	3 447(3)
C(8)	−525(3)	−4 001(6)	3 088(3)
C(8a)	−854(2)	−2 745(6)	2 824(2)
C(9)	−1 369(3)	−2 938(8)	2 395(3)
C(10)	−1 661(2)	−1 787(9)	2 078(3)
C(10a)	1 431(2)	−302(6)	2 103(2)
C(11)	−1 695(2)	875(8)	1 674(3)
C(12)	−1 447(2)	2 204(8)	1 628(3)
C(13)	−923(2)	2 431(6)	2 000(2)
C(14)	−673(2)	1 328(5)	2 444(2)
C(14a)	−916(1)	−53(5)	2 537(2)
C(14b)	−647(2)	−1 272(5)	2 972(2)
C(14c)	−155(2)	−1 110(5)	3 503(2)
C(14d)	8(1)	223(5)	3 926(2)
H(1)	−73(2)	125(4)	375(2)
H(2)	−41(2)	328(5)	447(2)
H(3)	46(2)	367(6)	509(3)
H(4)	109(2)	162(5)	508(2)
H(5)	125(2)	−71(6)	471(3)
H(6)	94(2)	−310(6)	408(3)
H(7)	26(2)	−482(8)	364(3)
H(8)	−73(2)	−497(7)	291(3)
H(9)	−156(2)	−407(7)	230(3)
H(10)	−203(2)	−182(6)	184(3)
H(11)	−204(2)	65(6)	139(2)
H(12)	−159(2)	303(5)	135(2)
H(13)	−73(2)	336(5)	190(2)
H(14)	−34(1)	144(4)	270(2)

(iii) Molecule (II)

	x	y	z
C(1)	1 952(2)	6 156(5)	5 067(2)
C(2)	1 691(2)	4 963(6)	5 277(3)
C(3)	1 571(3)	4 979(13)	5 937(4)
C(4)	1 687(3)	6 207(14)	6 352(4)
C(4a)	1 934(2)	7 464(9)	6 150(3)
C(5)	1 994(4)	8 889(16)	6 512(5)
C(6)	2 147(4)	10 103(13)	6 250(7)
C(6a)	2 325(2)	10 107(8)	5 617(5)
C(7)	2 433(7)	11 508(7)	5 300(5)
C(14c)	2 367(2)	8 709(5)	5 284(3)
C(14d)	2 108(2)	7 420(6)	5 502(2)
H(1)	203(1)	614(5)	456(2)
H(2)	152(2)	406(6)	488(2)
H(3)	143(3)	1 415(8)	610(4)
H(4)	158(2)	606(7)	681(3)
H(5)	184(3)	856(8)	693(4)
H(6)	209(4)	1 088(12)	651(5)
H(7)	244(5)	238(16)	562(7)

respectively. The intensity data were not corrected for absorption due to the small values of μ.

The crystal-packing modes of [6]-, [7]-, [10]- and [11]-helicene are analysed from the atomic co-ordinates given in refs. 9, 12—14.

The final atomic parameters with estimated standard deviations are listed for each of the structures in Table 1. Observed and calculated structure amplitudes and thermal parameters of the atoms are tabulated in Supplementary Publication No. SUP 23277 (25 pp.).*

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

DISCUSSION

Molecule (II) of form B resides on a site of two-fold symmetry, while molecule (I) of form B and the unique molecule, (III), of form A are located at a general position. As is shown by the bond lengths and angles (Table 2), the molecules in a general position have approximate

TABLE 2

Bond distances (Å) and angles (°)

	Crystal A Molecule (III)	Crystal B Molecule (I)	Crystal B Molecule (II)
C(1)–C(2)	1.373(3)	1.361(6)	
C(13)–C(14)	1.371(3)	1.365(6)	1.374(6)
C(2)–C(3)	1.397(3)	1.393(7)	
C(12)–C(13)	1.396(4)	1.395(7)	1.395(8)
C(3)–C(4)	1.357(4)	1.344(8)	
C(11)–C(12)	1.351(4)	1.361(8)	1.350(1)
C(4)–C(4a)	1.409(3)	1.406(7)	
C(11)–C(10a)	1.417(4)	1.412(7)	1.394(11)
C(5)–C(4a)	1.423(3)	1.420(7)	
C(10)–C(10a)	1.440(4)	1.448(8)	1.441(11)
C(5)–C(6)	1.335(4)	1.324(8)	
C(9)–C(10)	1.330(5)	1.336(8)	1.229(14)
C(6)–C(6a)	1.423(4)	1.427(7)	
C(9)–C(8a)	1.420(4)	1.408(8)	1.418(13)
C(7)–C(6a)	1.412(4)	1.407(8)	
C(8)–C(8a)	1.433(4)	1.427(7)	1.447(9)
C(1)–C(14d)	1.410(3)	1.407(6)	
C(14)–C(14a)	1.409(3)	1.413(6)	1.408(6)
C(14c)–C(14d)	1.455(3)	1.449(6)	
C(14a)–C(14b)	1.456(3)	1.449(6)	1.445(6)
C(14d)–C(4a)	1.419(3)	1.431(6)	
C(14a)–C(10a)	1.415(3)	1.418(6)	1.441(7)
C(14c)–C(6a)	1.416(3)	1.419(6)	
C(14b)–C(8a)	1.422(3)	1.420(6)	1.420(7)
C(7)–C(8)	1.339(4)	1.346(8)	1.301(18)
C(14b)–C(14c)	1.443(3)	1.445(6)	1.439(10)
C(14d)–C(1)–C(2)	121.8(2)	121.3(5)	
C(14a)–C(14)–C(13)	122.2(2)	123.2(4)	121.9(4)
C(1)–C(2)–C(3)	120.5(2)	121.7(6)	
C(14)–C(13)–C(12)	119.7(2)	118.9(5)	120.2(7)
C(2)–C(3)–C(4)	119.3(2)	118.7(6)	
C(13)–C(12)–C(11)	120.0(3)	120.7(5)	119.6(8)
C(3)–C(4)–C(4a)	121.5(2)	122.1(5)	
C(12)–C(11)–C(10a)	121.5(3)	120.8(5)	122.2(7)
C(4)–C(4a)–C(14d)	119.8(2)	119.4(5)	
C(11)–C(10a)–C(14a)	119.0(2)	119.6(5)	119.3(6)
C(4a)–C(14d)–C(1)	116.8(2)	116.7(4)	
C(10a)–C(14a)–C(14)	117.1(2)	116.5(4)	116.4(5)
C(4)–C(4a)–C(5)	120.2(2)	121.9(5)	
C(11)–C(10a)–C(10)	122.0(3)	121.2(5)	124.8(8)
C(1)–C(14d)–C(14c)	123.3(2)	123.3(4)	
C(14)–C(14a)–C(14b)	122.8(2)	123.9(4)	122.9(4)
C(14d)–C(14c)–C(14b)	125.1(2)	125.2(4)	124.9(6)

TABLE 2 (continued)

	Crystal A Molecule (III)	Crystal B Molecule (I)	Crystal B Molecule (II)
C(14a)–C(14b)–C(14c)	125.3(2)	124.3(4)	
C(14d)–C(14c)–C(6a)	116.4(2)	116.5(4)	117.9(6)
C(14a)–C(14b)–C(8a)	116.7(2)	117.7(4)	
C(14b)–C(14c)–C(6a)	118.4(2)	118.2(4)	117.1(6)
C(14c)–C(14b)–C(8a)	117.9(2)	117.7(4)	
C(14c)–C(6a)–C(6)	120.1(2)	119.9(5)	118.2(8)
C(14b)–C(8a)–C(9)	119.9(3)	119.6(5)	
C(14c)–C(6a)–C(7)	119.6(3)	119.7(5)	121.0(9)
C(14b)–C(8a)–C(8)	118.9(3)	118.9(5)	
C(4a)–C(5)–C(6)	119.8(2)	121.3(6)	123.0(1)
C(10a)–C(10)–C(9)	120.8(2)	119.9(5)	
C(6a)–C(7)–C(8)	121.1(3)	120.5(6)	120.4(5)
C(8a)–C(8)–C(7)	121.1(3)	121.5(6)	
C(5)–C(6)–C(6a)	122.2(2)	121.5(6)	123.0(1)
C(10)–C(9)–C(8a)	121.7(3)	122.4(6)	
C(6)–C(6a)–C(7)	120.3(3)	120.3(6)	120.7(8)
C(9)–C(8a)–C(8)	121.1(3)	121.4(6)	
C(14d)–C(4a)–C(5)	119.8(2)	118.6(5)	115.7(8)
C(14a)–C(10a)–C(10)	118.6(3)	119.1(5)	
C(4a)–C(14d)–C(14c)	119.6(2)	119.8(4)	120.2(5)
C(10a)–C(14a)–C(14b)	119.7(2)	119.1(4)	

C_2 symmetry. The molecular structures are generally similar among molecules (I)—(III), and the bond distances follow the classification of medium, inner, external, and radial bonds described in the detailed survey of molecular structures of helicenes reported recently.[15] The geometry of molecule (II) is slightly different from the other two (Table 2), although the differences may not be so significant on account of the large standard deviations of the bond lengths, particularly of those involving the inner helix atoms.

The relevant intramolecular atomic distances and torsion angles are listed in Table 3. The closest intramolecular carbon · · · carbon distance occurs between C(1) and C(14) and their values for molecules (I)—(III) are slightly larger than the closest contact distances of 2.892, 2.910, and 2.906 Å, observed for [7]helicene [9] and slightly smaller than the C(1) · · · C(8′) distances of 2.931 and 2.971 Å for (+)- [3] and (±)-BN.[16]

The deviations of the torsion angles from the ideal value of 180 or 0° for regular aromatic hydrocarbons are much larger in the inner than in the outer helices (Table 3). In particular, the torsion angle at the central ring, C(14a)-C(14b)-C(14c)-C(14d), is as large as 30°, very similar to the value observed for the corresponding angle of [6]helicene.[15] The mean plane was calculated for each of the benzoid rings, and the dihedral angles between the planes are given in Table 4, for each of the molecules. The terminal rings, A and E, have good planarity, while the central ring is the most puckered. The angles between neighbouring planes are ca. 12—13°, which seems to be common to all members of the series

higher than [5]helicene. In the case of benzo[c]phen-anthrene ([4]-helicene), intramolecular interaction is much smaller as indicated by the rapid racemization, although the structure already shows a helical geo-metry.[17] The dihedral angles between adjacent rings are

TABLE 3

Relevant non-bonded intramolecular atomic distances (Å) and torsion angles (°)

	Crystal A Molecule (III)	Crystal B Molecule (I)	Crystal B Molecule (II)
C(1) · · · C(14)	2.921	2.954	2.925 ᵃ
C(1) · · · C(14a)	3.146	3.154	
			3.128
C(14) · · · C(14d)	3.152	3.160	
C(1) · · · C(14b)	3.083	3.071	
			3.058
C(14) · · · C(14c)	3.080	3.073	
C(14a) · · · C(14d)	3.173	3.167	3.149
C(1) · · · H(14)	2.594	2.551	
			2.579
C(14) · · · H(1)	2.602	2.589	
C(14a) · · · H(1)	2.624	2.576	
			2.553
C(14d) · · · H(14)	2.614	2.585	
C(14b) · · · H(1)	2.802	2.747	
			2.756
C(14c) · · · H(14)	2.768	2.734	
C(14b) · · · H(14)	2.660	2.633	
			2.722
C(14c) · · · H(1)	2.702	2.683	
H(1) · · · H(14)	2.60	2.50	2.64 ᵃ
C(1)–C(14d)–C(14c)–C(14b)	18.4(1)	17.0(3)	−19.0(3) ᵃ
C(14d)–C(14c)–C(14b)–C(14a)	27.9(1)	32.0(3)	−29.7(3) ᵃ
C(14c)–C(14b)–C(14a)–C(14)	20.1(1)	17.6(3)	−19.1(3) ᵃ
C(3)–C(4)–C(4a)–C(5)	−171.2(3)	−173.5(6)	
			169.8(9)
C(10)–C(10a)–C(11)–C(12)	−169.4(3)	−171.1(6)	
C(4)–C(4a)–C(5)–C(6)	169.1(3)	167.2(6)	
			−168.4(10)
C(9)–C(10)–C(10a)–C(11)	167.5(3)	168.7(6)	
C(5)–C(6)–C(6a)–C(7)	−174.2(3)	−170.7(6)	
			172.7(10) ᵃ
C(8)–C(8a)–C(9)–C(10)	−176.2(3)	−172.2(6)	
C(6)–C(6a)–C(7)–C(8)	177.0(3)	176.7(6)	
			−176.1(10) ᵃ
C(7)–C(8)–C(8a)–C(9)	177.2(3)	174.3(6)	

ᵃ Some atoms are related by C_2 symmetry.

8.0, 9.3, and 10.2°, smaller than the other members of the helicene group, and the dihedral angle between the two terminal rings is 27.4°. A cyclic intermediate was sug-gested[2] for the racemization of [5]helicene.

mistake probably arose from the fact that only the $(h\ 0\ l)$ zone was studied intensively before.[8]

Crystal Packing of Form A.—The crystal structure of form A is shown in Figure 1, as a projection along the crystal a axis. The C_2 axis of the molecule is almost parallel to the crystal c axis throughout the structure. There are homochiral layers parallel to the crystal ab plane with alternate layers of R- and S-molecules along the c axis. Although the molecules are aligned with their C_2 axes collinear, they are related by inversion centres but not by translation along the rotation axis

TABLE 4

Dihedral angles between benzene-ring planes

	A	B	C	D
Crystal A, molecule (III)				
B	11.9			
C	24.0	12.3		
D	35.4	24.1	11.9	
E	47.3	36.6	24.8	13.0
Crystal B, molecule (I)				
B	11.0			
C	25.5	14.6		
D	39.1	28.2	13.6	
E	50.6	39.9	25.3	12.2
Crystal B, molecule (II)				
B	12.5			
C	24.9	12.8		
D	37.5	25.6	12.8	
E	48.9	37.5	24.9	12.5

hence there is no close contact along the C_2 axis similar to that observed in the (+)-BBN crystal structure. The closest intermolecular C · · · C contact is outstanding between neighbouring molecules related by the a axis translations ($a = 5.815$ Å). The majority of close C · · · C and C · · · H contacts are between homochiral molecules, while all the shortest H · · · H distance are observed between heterochiral molecules belonging to neighbouring ab planes. The mean planes of molecules related by a 2_1 screw axis form a dihedral angle of 82.7° and the usual herring-bone pattern is observed in the ab plane.

Crystal Packing of Form B.—The C_2 axis of molecule (I) and (II) is nearly and exactly parallel to the crystal b axis, respectively, the latter being required by crystal symmetry. As was discussed previously,[4] homochiral molecules with the morphology of a helical segment pack
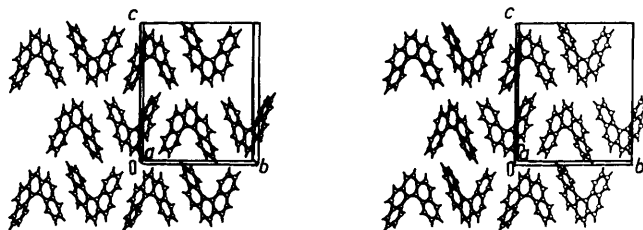

FIGURE 1 Projection of [5]helicene, form A, along the a axis

The structure of form B does not agree with that re-ported previously in a sense that all the y co-ordinates of molecule (II) have opposite sign. Hence the chirality of molecule (II) only is reversed at a particular site. The

well with their C_2 axes parallel to each other, inserting the central ring, or the ethano-bridge in case of BBN, into a dihedral volume of an immediate neighbour molecule. This pattern is observed in the crystal structure of form

B. The repetition period along the b axis is 8.898 Å, which is much longer than the corresponding period of 8.142 Å in optically active BBN.[4] This is due to the fact that the dihedral void volume produced by the non-planar [5]helicene is much smaller than that of bridged or non-bridged 1,1'-binaphthyl. Nonetheless, one of the

C(2) · · · C(7) contact, there is no close contact between the molecules (II) (SUP 23277). The too close C · · · C contact reported by previous authors [8] may be due to the reversed absolute configuration of molecules (II).

Comparison of Crystal Packing Mode, including Other Members of Helicene Series.—Crystal A is more dense than
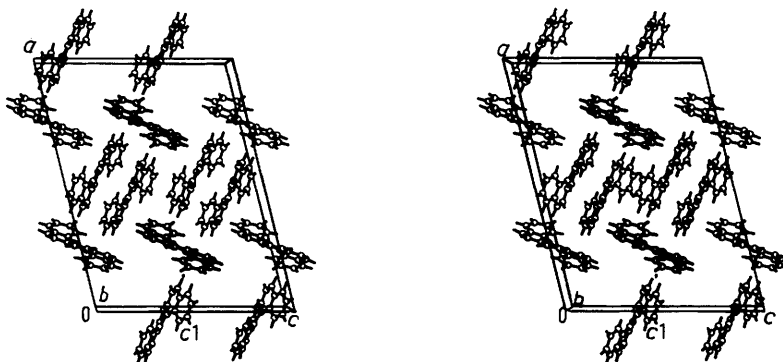
FIGURE 2   Projection of [5]helicene, form B, along the b axis

closest intermolecular contacts involving molecule (II) is found in this type of packing (SUP 23277).

There are layers consisting solely of molecule (I) and of molecule (II), parallel to the crystal ab plane. In the layer composed of molecule (I), molecules of opposite chirality are related by inversion centres along the c-axis, and the homochiral molecules by the b-axis translation (Figure 2). The layers of molecule (II), on the other hand, are composed of homochiral molecules related by a translation and two-fold screw-axis along b. The layers of R-molecules and those of S alternate, with the layer of molecule (I) between them.

crystal B, though the difference is only 1.5%. In both structures, the molecular C_2 axes are nearly parallel and the mean molecular planes are either parallel or nearly orthogonal to each other; however, the crystal packing modes as a whole are quite different. Despite the difference in the packing modes, the molecular structures are similar, showing that the crystal field does not affect the molecular geometry very much.

Table 5 lists the crystal data of helicenes. According to Kitaigorodsky,[18] the organic molecules with C_2 symmetry are optimally packed in the space group of $P2_12_12_1$ for the optically active structure and of either $C2/c$ or

TABLE 5

Crystal data of [n]helicenes

n	Modification	Space group	Z	a (Å)	b (Å)	c (Å)	β (°)	ρ (g cm^{-3})	Reference
4		$P2_12_12_1$	4	14.666	14.157	5.785		1.262	17
5	form A	$P2_1/c$	4	5.185	14.178	17.498	94.41	1.285	This work
	form B	$A2/a$	12	26.013	8.898	19.494	103.91	1.266	This work
6		$P2_12_12_1$	4	17.511	13.156	7.344		1.275	14
7	form A	$P2_1$	4	14.022	15.094	9.221	93.20	1.288	9a
	form B	$P2_1/c$	4	8.112	11.504	21.584	106.23	1.30	9b
10		$P2_1$	2	10.090	13.594	10.782	116.74	1.455	12
11		$P2_1$	2	10.01	14.35	10.92	116.7	1.371	13

The part of the packing mode of molecule (I) related by inversion centres, where the shortest intermolecular contacts are found (SUP 23277), is somewhat similar to that of racemic 1,1'-binaphthyl.[16] The molecules (I) and (II) are orientated nearly orthogonally, with parallel C_2 axes but average molecular planes form 87° to each other. There are some close C · · · C contacts between molecules (I) and (II) in addition to the one between molecules (I) mentioned above; however, most of the closest H · · · H contacts are between molecule (I) and molecule (II). Molecule (II) is surrounded by molecules (I) apart from a short b-axis translation, hence with the exception of the

$Pbcn$ for the racemic structure. The crystals of (+)-BBN, ($\pm$)-BBN, and (+)-BN do not conform to the maximum density criterion, crystallizing in a higher crystal system of trigonal, tetragonal, and tetragonal respectively. Crystal B of [5]helicene, on the other hand, conforms to the criterion and $P2_12_12_1$ ([4]- [17] and [6]-helicene [14]), $P2_1/c$ (form A of [5]- and form B of [7]-helicene [9b]) and $P2_1$ (form A of [7]-,[9a] [10]-,[12] and [11]-helicene [13]) are the space groups of the closest packing for molecules of general morphology.

From the crystal packing point of view, helicenes may be classified into two categories. One includes helicenes

of lower number. The molecule has a morphology of a helical segment but is not sufficiently long to form more than one turn of a helix. The other involves the higher helicenes, where molecules have a true helical morphology, consisting of more than one turn. For this type of helicene, the packing of helices of opposite chirality
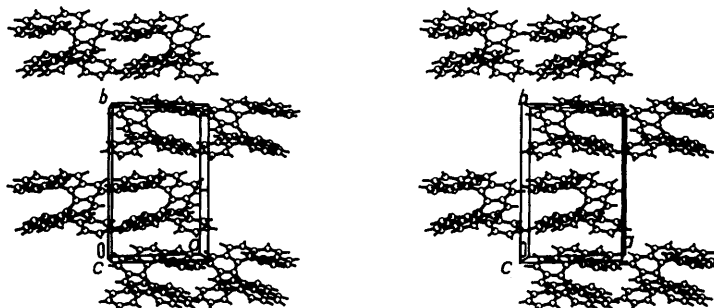
the crystal c axis at $x \sim 0.25$, $y \sim 0.42$, and a 2_1 screw axis along the a axis at $y \sim 0.01$, $z \sim 0.20$. The racemic structure of [7]helicene is slightly more dense than the corresponding chiral one. There is no similarity in the packing mode between the form A of [5]- and form B of [7]helicene, even in the same space group of $P2_1/c$.

FIGURE 3   Projection of [11]helicene along the c axis

seems to be not so efficient. Homochiral helices are optimally packed when their helical axes are parallel, side by side, but the translation direction relating these helices is not perpendicular to the helical axes so that the insertion of a helical segment of a molecule into a helical void volume of an immediate neighbour is possible. The packing patterns of [10]- and [11]-helicenes resemble one another and are representative of this packing pattern [12,13] (Figure 3). In both structures, the helical axis is not parallel to the crystal 2_1 axis, forming an angle of ca. 60° between the helical axes related by a 2_1 screw.

The helicenes of smaller n have relatively large and accessible dihedral volumes. The insertion of part of a molecule into the dihedral void volume of a neighbouring molecule is possible by a slight adjustment of the relative orientation of the molecules. They may be related by a translation along the molecular C_2 axis, an inversion centre, or by a 2_1 screw axis. This may be the reason that racemic crystals are formed by the relatively small helicenes such as [5]- and [7]-helicenes.

When grown from racemic solution, [6]helicene crystallizes in the chiral space group $P2_12_12_1$;[14] however, the dissolved single crystals display optical resolutions corresponding to an enantiomeric excess of only ca. 5%. This puzzling observation was recently explained [19,20] as a lamellar twinning along the a axis. The packing pattern of the chiral crystal and that of a boundary of the proposed twinned structure [enantiomorphous structures are placed side by side around the bc plane, with a translation of ($\frac{1}{2}$, 0, $\frac{1}{2}$)] are very similar.[19]

There are two modifications in [7]helicenes. The crystal structure of space group $P2_1$ has two independent molecules and the packing mode generally resembles that of [6]helicene in the space group $P2_12_12_1$. Although the crystals of [7]helicene belong to the monoclinic system, one can assume an approximate 2_1 screw axis parallel to

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