toinduced diffusion and clustering of the silver atoms can all be qualitatively understood. Although the successful interpretation of the absorption and emission spectra suggests that the main features of the potential energy surfaces are adequately described, the data do not permit a conclusive demonstration of the importance of the Jahn-Teller effect. The vibronic model is attractive, however, because unlike the crystal field model,[13] it does not require the assumption of lower than octahedral symmetry for the ground-state silver atom trapping site. This is an inherent difficulty of the crystal field approach, because it is not readily apparent why substitutionally incorporated ^{2}S Ag atoms should occupy axially distorted tetradecahedral trapping sites.

It is clear that many problems remain for future research in this area. In particular, the temperature and concentration dependence of the emission spectra, the polarization properties, and the competition between $^2D \rightarrow {}^2S$ and "relaxed" $^2P \rightarrow {}^2S$ emission require further study. It is hoped that continuing research will further elucidate the photoprocesses of matrix-isolated silver atoms. An extension to silver cluster species and to other metal and matrix systems is planned for the future.

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Solid-State Resolution of Binaphthyl: Crystal and Molecular Structures of the Chiral (A)[1] Form and Racemic (B)[1] Form and the Study of the Rearrangement of Single Crystals. Requirements for Development of Hemihedral Faces for Enantiomer Identification

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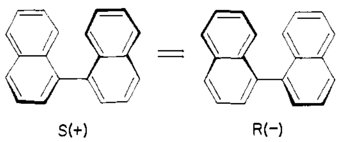
Abstract: The conversion in the solid state of single crystals of the racemic (low-temperature) form of 1,1′-binaphthyl to the chiral (high-temperature) form, shown previously by Pincock and Wilson to occur in bulk samples with formation of a great predominance of one enantiomer, has been studied. When a large single crystal is subjected to temperatures and times which have been shown to cause rearrangement of crystalline racemic binaphthyl to the chiral form, crystals of the chiral form can be seen growing in the vicinity of the parent crystal but Weissenberg photographs of the parent still show the undistorted reflections of the low-temperature racemic starting material. A reaction front leading to the production of an opaque product is observed under the appropriate conditions. Infrared and X-ray powder analyses of the product show evidence of only a few percent of the chiral product. We conclude that, at least under our reaction conditions, the major reaction pathway is not a solid-solid transformation but a solid-vapor-solid process. The crystal structure of chiral 1,1′-binaphthyl has been determined by X-ray methods. Colorless tetragonal bipyramids have $a = 7.181$ (2) Å and $c = 27.681$ (10) Å, and the structure was refined to an R factor of 0.043 on the basis of 978 nonzero reflections. A new set of data for the racemic (B) form which has been determined previously was collected, and a refinement of the structure has been carried out. The conditions for the occurrence and recognition of hemihedral faces in common chiral space groups for organic compounds are discussed.

Introduction

By virtue of restricted rotation about the bond joining the aromatic ring systems, 1,1′-binaphthyl (I) exists in its stable



conformation as a chiral molecule. In the crystalline state it exists in two forms: the A or higher melting (159 °C) and the B or lower melting (145 °C). The B form, whose structure was determined by Kerr and Robertson,[3a] following earlier work by Brown, Trotter, and Robertson,[3b] consists of racemic crystals (space group $C2/c$) whereas the A form, whose structure has not previously been reported, was known to crystallize as a conglomerate of chiral crystals. The racemic B form is transformed on heating in the solid state to the chiral A form. An elegant and detailed study by Pincock and collaborators[4] has elucidated many features of this conversion. It is of particular interest that with ingeneously devised experimental conditions, Pincock and Wilson[4a] were able to direct the reaction to produce from essentially racemic B form the chiral A form with a high predominance of one of the two enantiomers.

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[1] The racemic, low temperature form of 1,1′-binaphthyl has been called the "B" form by previous workers.[3]

[2] (a) University of Illinois. (b) 3M Company.

[3] (a) K. A. Kerr and J. M. Robertson, *J. Chem. Soc. B*, 1146 (1969); (b) W. A. C. Brown, J. Trotter, and J. M. Robertson, *Proc. Chem. Soc., London*, 115 (1961).

[4] (a) K. R. Wilson and R. E. Pincock, *J. Am. Chem. Soc.*, **97**, 1474 (1975); (b) K. R. Wilson and R. E. Pincock, *Can. J. Chem.*, **55**, 889 (1977); (c) R. E. Pincock, R. P. Bradshaw, and R. R. Perkins, *J. Mol. Evol.*, **4**, 67 (1974); (d) R. E. Pincock, R. R. Perkins, A. S. Ma, and K. R. Wilson, *Science*, **174**, 1018 (1971).

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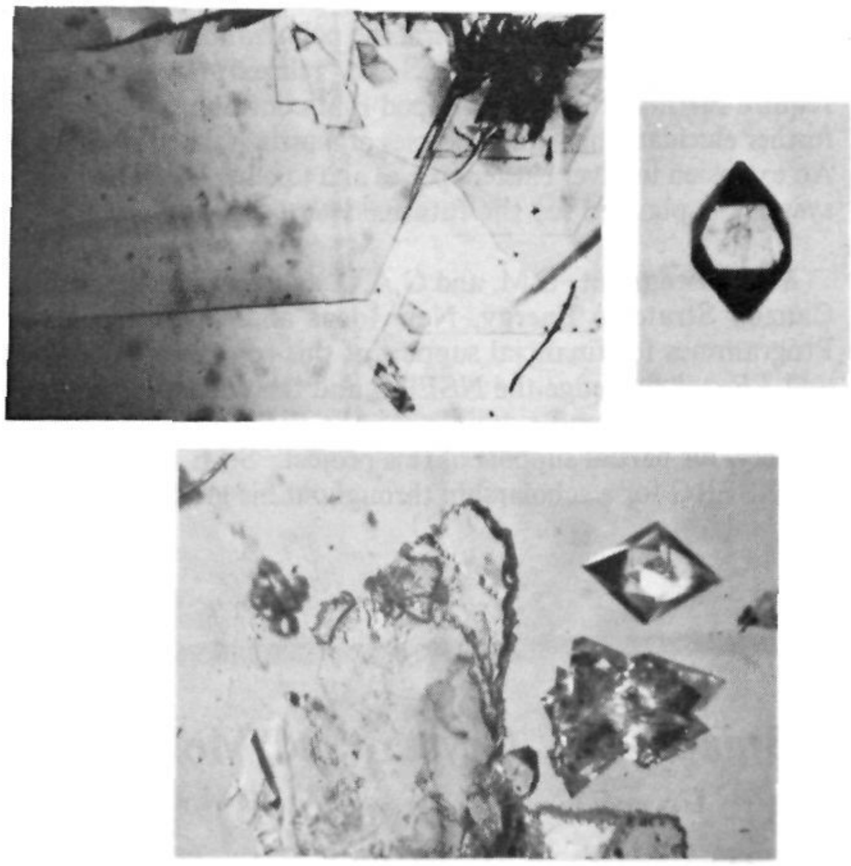

Figure 1. Low- and high-temperature forms of 1,1′-binaphthyl: upper left, very thin plates of the low-temperature form (acetone); upper right, the tetragonal-bipyramidal high-temperature form (recrystallization from acetone); bottom, formation of crystals of the high-temperature form (right) when a thin plate of the low-temperature form is heated (24 h, 130 °C). Note the thickening of the edge of the original crystal of the low-temperature form at the left of the photograph.

We now report the crystal structure of the higher melting A form and a redetermination of the structure of the B form and also our observations of the transformation of single crystals of B to A. We provide evidence that, under our conditions, the predominant pathway is a solid–gas–solid rather than a solid–solid transformation.

A question which has arisen here and is of more general interest is when can one expect to observe hemihedral faces (as first observed by Pasteur[5] with sodium ammonium tartrate dihydrate). It appears not to have been pointed out previously that certain restrictions to the Miller indices of the crystal faces are imposed if hemihedral faces are to be observed. These limitations are discussed for the A form of binaphthyl and also for space groups more common among chiral organic crystals.

Experimental Section

Crystal Structure Determination of the A Form of 1,1′-Binaphthyl. Crystallization from acetone gave the compound as beautifully formed tetragonal bipyramids (see Figure 1). A crystal 0.5 × 0.5 × 0.48 mm was chosen for the X-ray studies which were carried out at ambient room temperature (22–25 °C).

Crystal Data: $C_{20}H_{14}$, $M_r = 254.4$, tetragonal, $P4_12_12$ (or $P4_32_12$), $a = 7.181\ (2)$ Å, $c = 27.681\ (10)$ Å, $V = 1427.6$ Å^3, $D_m = 1.175$ g cm^{-3}, $Z = 4$, $D_c = 1.18$ g cm^{-3}, $F(000) = 536$, μ(Mo Kα) = 0.7 cm^{-1}.

Unit cell dimensions were obtained on a Syntex P2$_1$ diffractometer (Mo Kα, $\lambda = 0.71069$ Å) by a least-squares fit to the settings for 15 reflections. Intensity data were collected also by using Mo Kα radiation, in the 2θ scan mode. Reflections in the octants $h,\pm k,l$ and $\bar{h},k,l$ were collected to $2\theta = 55°$. After averaging symmetry-equivalent reflections, a total of 1058 unique reflections was obtained; of these 978 were considered above zero at the $2\sigma(I)$ significance level. There was no evidence for crystal decomposition. Lorentz and polarization corrections were applied, but no correction was made for extinction or absorption.

The structure was solved in the space group $P4_12_12$ by using the MULTAN series of programs.[6] Hydrogen atoms were included at positions calculated by standard criteria but their parameters ($B_{iso} = 7.0$ Å^2) were not varied in the refinement. Full-matrix least-squares refinement on the positional and anisotropic thermal parameters for the carbon atoms converged with $R = 0.043$, $R_2 = 0.050$, and $[\sum w|F_o| - |F_c||^2/(m-n)]^{1/2} = 1.68$, on the basis of the 978 nonzero reflections. The largest electron density on a final difference map was 0.13 e Å^{-3}. The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, and the scattering curves were taken from the analytical expressions in the International Tables for X-ray Crystallography. The final atomic coordinates are presented in Table I.

Table I. Final Atomic Coordinates for the Chiral, Trans, A Form of Binaphthyl[a,b]

atom	*x*	*y*	*z*
C(1)	0.4855 (3)	0.3742 (3)	0.25830 (7)
C(2)	0.4665 (4)	0.2080 (3)	0.23451 (9)
C(3)	0.3354 (4)	0.0743 (4)	0.24926 (10)
C(4)	0.2249 (4)	0.1067 (4)	0.28800 (9)
C(4A)	0.2398 (3)	0.2757 (3)	0.31407 (7)
C(5)	0.1308 (4)	0.3115 (4)	0.35551 (9)
C(6)	0.1488 (4)	0.4725 (4)	0.38076 (10)
C(7)	0.2748 (4)	0.6093 (4)	0.36530 (8)
C(8)	0.3832 (3)	0.5810 (3)	0.32535 (7)
C(8A)	0.3706 (3)	0.4118 (3)	0.29876 (7)
H(2)	0.548 (0)	0.181 (0)	0.2060 (0)
H(3)	0.324 (0)	−0.045 (0)	0.2310 (0)
H(4)	0.132 (0)	0.011 (0)	0.2983 (0)
H(5)	0.038 (0)	0.216 (0)	0.3665 (0)
H(6)	0.072 (0)	0.494 (0)	0.4104 (0)
H(7)	0.285 (0)	0.729 (0)	0.3837 (0)
H(8)	0.472 (0)	0.680 (0)	0.3147 (0)

[a] The hydrogen atoms were given the numbers of the atoms to which they were attached. [b] The positions and thermal parameters of the hydrogen atoms were not varied during the refinement.

Table II. Final Atomic Coordinates for the Racemic, Cis, B Form of Binaphthyl[a]

atom	*x*	*y*	*z*
C(1)	0.464 49 (8)	0.3931 (3)	0.2471 (2)
C(2)	0.439 05 (9)	0.5511 (3)	0.3106 (2)
C(3)	0.371 73 (10)	0.5604 (4)	0.3047 (2)
C(4)	0.329 82 (9)	0.4120 (4)	0.2353 (2)
C(4A)	0.353 36 (8)	0.2449 (3)	0.1682 (2)
C(5)	0.310 44 (9)	0.0876 (4)	0.0952 (2)
C(6)	0.333 69 (9)	−0.0699 (4)	0.0286 (2)
C(7)	0.399 97 (9)	−0.0776 (3)	0.0324 (2)
C(8)	0.442 79 (8)	0.0690 (3)	0.1021 (2)
C(8A)	0.420 72 (8)	0.2354 (3)	0.1731 (2)
H(2)	0.471 1 (9)	0.665 (3)	0.371 (2)
H(3)	0.356 1 (9)	0.677 (3)	0.349 (2)
H(4)	0.276 7 (8)	0.408 (3)	0.223 (2)
H(5)	0.262 2 (9)	0.093 (3)	0.094 (2)
H(6)	0.304 4 (10)	−0.181 (3)	−0.016 (2)
H(7)	0.415 8 (10)	−0.188 (4)	0.001 (2)
H(8)	0.492 2 (8)	0.057 (3)	0.109 (2)

[a] The hydrogen atoms are given the number of the carbon atoms to which they are attached.

The Crystal Structure Determination of the B Form of Binaphthyl

Crystals of the racemic or B form of binaphthyl were obtained as thick diamond-shaped plates from benzene. A trapezoidal section of a large diamond was cut for use in this study. Its dimensions were 1.7 × 1.0 × 0.30 mm.

Crystal Data: $C_{20}H_{14}$, $M_r = 254.4$, monoclinic, $C2/c$, $a = 21.126\ (2)$ Å, $b = 6.342\ (1)$ Å, $c = 10.218\ (5)$ Å, $\beta = 105.19\ (2)°$, $V = 1321.1$, $D_m = 1.30$ g cm^{-3},[3] $Z = 4$, $D_c = 1.279$ g cm^{-3}, $F(000) = 536$, μ(Cu Kα) = 5.6 cm^{-1}.

Data collection and the determination of the unit cell parameters were carried out on a Nonius Cad-4 diffractometer, at ambient room temperature. Reflections in the octants $\pm h,\pm k,l$ were collected up to $2\theta = 150°$, and symmetry equivalent reflections were averaged to give 1481 unique reflections with 1164 observed ($>3\sigma(I)$). Lorentz and polarization corrections were applied; an extinction coefficient was applied in the latter stages of refinement, but no absorption correction was applied.

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[5] See T. M. Lowry, "Optical Rotatory Power", Longmans, Green, and Co., London, 1935, reprinted by Dover Publications, Inc., 1964, p 25.

[6] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst., Sect A*, *A27*, 368 (1971). The structure of the chiral (A) form was solved on the version of MULTAN incorporated in the EXTL Syntex System; that of the racemic (B) form on the version incorporated in the Enraf-Nonius Structure Determination Package.

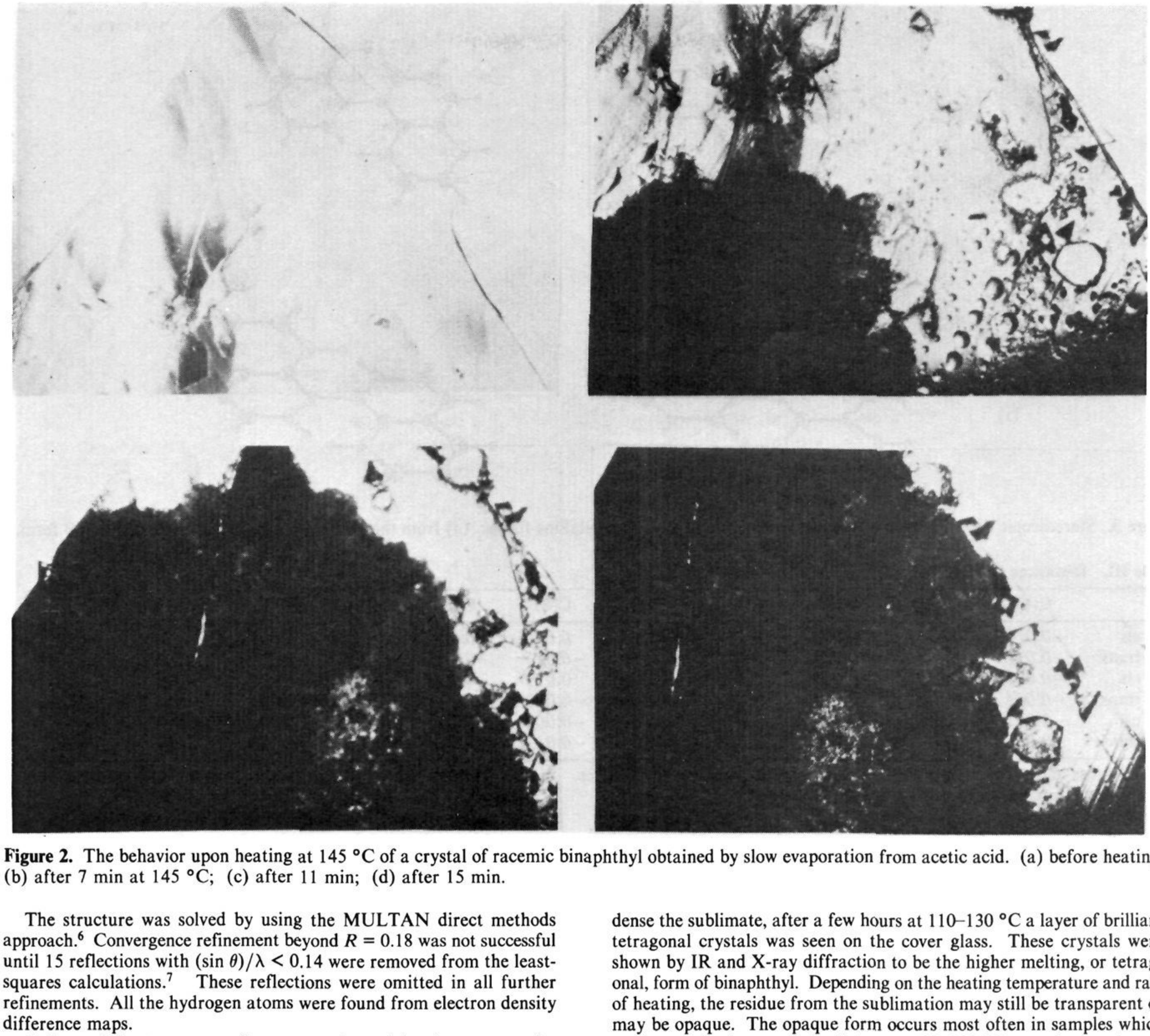

Figure 2. The behavior upon heating at 145 °C of a crystal of racemic binaphthyl obtained by slow evaporation from acetic acid. (a) before heating; (b) after 7 min at 145 °C; (c) after 11 min; (d) after 15 min.

The structure was solved by using the MULTAN direct methods approach.[6] Convergence refinement beyond $R = 0.18$ was not successful until 15 reflections with $(\sin\theta)/\lambda < 0.14$ were removed from the least-squares calculations.[7] These reflections were omitted in all further refinements. All the hydrogen atoms were found from electron density difference maps.

Full-matrix least-squares refinement on the positional parameters for all the atoms and on the anisotropic thermal parameters for the carbon atoms and the isotropic thermal parameters for the H atoms converged to $R = 0.050$ on the 1149 nonzero reflections with $(\sin\theta)/\lambda > 0.14$.[8] Unit weights were used in the refinement. The final atomic coordinates are presented in Table II.

Single-Crystal Thermal Transformation. Observations under the microscope of the thermal behavior of single crystals of racemic 1,1′-binaphthyl were made independently in the laboratories at the 3M Company (M.C.E.) and at the University of Illinois (R.B.K). To the extent that they overlapped, the two sets of observations were in agreement. Large (0.5 mg) single crystals of racemic 1,1′-binaphthyl grown (M.C.E.) from benzene or xylene were heated by a variety of techniques and at varying rates. In all cases at temperatures of about 120 °C, or higher, sublimation was observed to take place. Thermal gravimetric analysis of the weight loss by sublimation showed that a 0.63-mg flat diamond-shaped crystal heated at 20 °C/min up to 135 °C and held at that temperature for 16 h lost 1% by weight every 15 min. This rate was constant over the 16-h period. The crystal remained transparent and, even after this prolonged heat treatment, gave an undistorted single-crystal X-ray diffraction pattern which matched that of the racemic form. When crystals (or powders) of the racemic form were heated in an oven or on a hot stage and a cover glass was placed over the sample to condense the sublimate, after a few hours at 110–130 °C a layer of brilliant tetragonal crystals was seen on the cover glass. These crystals were shown by IR and X-ray diffraction to be the higher melting, or tetragonal, form of binaphthyl. Depending on the heating temperature and rate of heating, the residue from the sublimation may still be transparent or may be opaque. The opaque form occurs most often in samples which are heated for long periods of time at 120–130 °C or a shorter time at 140 °C. Infrared analysis and X-ray powder patterns show that the opaque crytals are still mainly racemic binaphthyl.[9]

In order to characterize the opaque crystals, we heated a single racemic crystal on a hot stage until it began to turn opaque (after 5 min at 140 °C). At this point the heating was stopped. A single-crystal Weissenberg X-ray pattern on the partly transformed crystal showed only the diffraction pattern of the racemate, with disorder apparent in the broadening of the diffraction spots to $\omega = 12°$. Several crystals of varying amounts of opacity were examined this way. They all gave essentially the same X-ray patterns with more or less disorder. A pattern of three unidentified low-angle spots showed up in *h0l* photographs of several of the crystals. The spots were of varying intensity relative to the racemate pattern but could not readily be identified either as reflections from another plane of the racemate or from the tetragonal form.

Crystals of the racemic form of 1,1′-binaphthyl were grown (R.B.K.) by slow evaporation of acetone, xylene, benzene, or acetic acid. The crystals from acetone were thin plates, whereas the other solvents gave large thick "diamond-shaped" crystals with rather poorly formed faces. When heated in the open on a Mettler hot stage to temperatures above 130 °C the thin crystals (acetone) vaporized before frontal migration or development of opacity of the initial crystal could be observed. However, when thicker single crystals (benzene or xylene) were sandwiched between a microscope slide and cover glass sealed on the edges with stopcock grease and heated above 130 °C, they were observed to diminish

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(7) These reflections (F_o and F_c in parentheses) were 200 (310, 324), 110 (80, 69), $11\bar{1}$ (662, 477), 400 (595, 483), 111 (350, 363), $20\bar{2}$ (829, 458), 002 (536, 482), 310 (292, 316), $31\bar{1}$ (95, 89), $40\bar{2}$ (214, 196), 202 (329, 379), $11\bar{2}$ (450, 453), 311 (323, 360), $31\bar{2}$ (806, 579), and 112 (1082, 491).

(8) When all nonzero reflections were included in the calculations, the R factor was 0.064.

(9) A powder diffractometer tracing of an opaque crystal of the heated racemic form which had undergone frontal migration showed only a trace of the tetragonal form as judged by minor peaks at $2\theta = 13.9$, 15.6, and 20.3° characteristic of the tetragonal form obtained by crystallization.

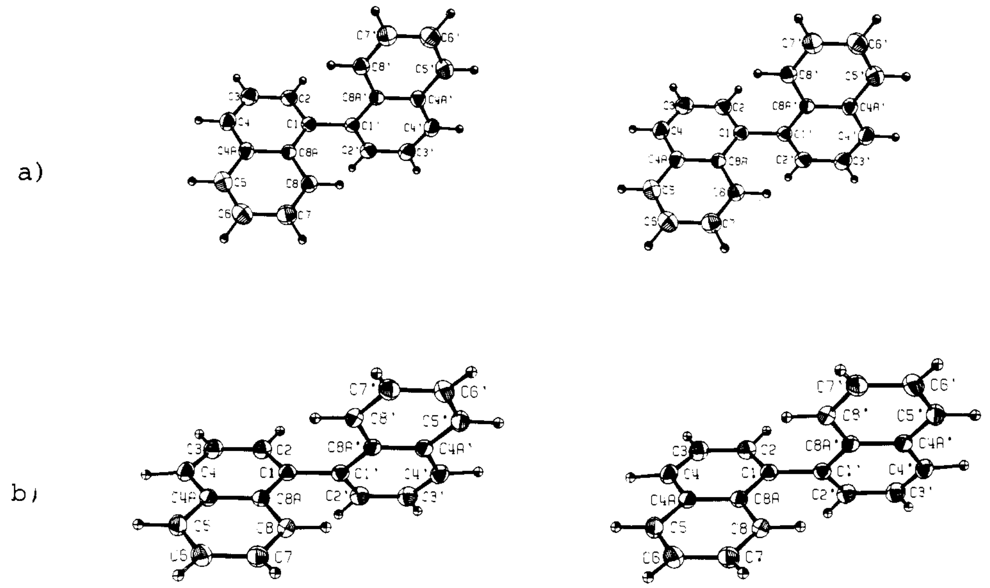

Figure 3. Stereoscopic drawings of the binaphthyl molecule in the two crystalline forms: (a) from the chiral A form, (b) from the racemic B form.

Table III. Distances (Å) of Atoms from Best Planes in Binaphthyl[a,b]

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(4A)	C(8A)	C(1')
cis	*−0.010*	*0.003*	*0.012*	*0.011*	*−0.013*	*0.000*	*0.012*	*0.007*	*−0.008*	*−0.009*	0.019
trans	*−0.012*	*−0.021*	*−0.001*	*0.015*	*−0.010*	*−0.035*	*−0.008*	*0.018*	*0.016*	*0.014*	−0.027
cis	*−0.001*	*−0.001*	*0.000*	*0.005*	−0.005	0.019	0.040	0.031	*−0.004*	*0.003*	0.036
trans	*−0.001*	*−0.004*	*0.004*	*0.002*	−0.050	−0.083	−0.044	0.001	*−0.005*	*0.005*	−0.004
cis	−0.001	0.022	0.040	0.035	*−0.004*	*−0.002*	*0.003*	*0.000*	*0.005*	*−0.004*	0.020
trans	−0.058	−0.077	−0.044	−0.006	*0.004*	*−0.012*	*0.003*	*0.006*	*0.006*	*−0.009*	−0.088

[a] Distances of atoms involved in the plane calculation are given in italics. [b] Atoms were weighted as $1/\sigma^2$, where σ is the standard deviation from the least-squares refinement.

into opaque masses with irregular surfaces. The characteristic tetragonal bipyramids of the product appeared throughout the sealed area. Thick crystals from acetic acid when heated to 143 °C formed an almost immediate front which advanced rapdily (22 min) across the crystal face leaving an opaque irregular surface surrounded by tetragonal crystals (Figure 2). The opaque mass melted at 158.4 °C, the melting point of the tetragonal form.

Results and Discussion

Thermal Rearrangement of Single Crystals of the Racemic to the Chiral Binaphthyl. Single crystals of the low-temperature form of binaphthyl as grown from solution are flat plates while the chiral, high-temperature stable form grows both from solution and by sublimation as quite characteristic tetragonal bipyramids (Figure 1). Visual microscopic observation (see Figure 2) of heated crystals of the low-temperature form under a microscope showed, under the appropriate conditions, nucleation with development of an opaque "front" followed by migration of the front through the crystal. At the same time the tetragonal bipyramids of the high-temperature form could be seen forming on the area of the microscope slide surrounding the crystal undergoing reaction. It was at first assumed that the migration of a reaction front was due to formation of the high-temperature form produced by a solid-solid transformation. That this is not the case was suggested from several lines of evidence. Wilson and Pincock[4b] had observed the rate of conversion of racemic binaphthyl to the chiral form at 135 °C and found that the times for 50% reaction ranged from 10 min (ground samples) to 45 min (reaction after sample stored for 6 weeks). These results can be compared with our work in which a single crystal heated at 135 °C for 16 h lost 1% of its weight every 15 min by sublimation and at the end of that time gave an undistorted X-ray diffraction pattern of the starting racemic form. A comparison of the rates of sublimation in the two experiments should take into account the difference in surface areas exposed. In our study, characteristic tetragonal bipyramids were regularly seen growing in other areas of any cavity containing heated crystals of the racemic form. While these tetragonal crystals sometimes appeared on surfaces of the racemic form, they showed no particular preference for nucleation at such surfaces. A comparison of the infrared spectrum and X-ray powder pattern with those of authentic low- and high-temperature forms of binaphthyl indicated that crystals even after passage of a reaction front consisted almost entirely of the low-temperature form with only traces of the high-melting form. We are unable to say at present what change is occurring in the crystal during a frontal migration. However, our observations provide strong support for the idea that the rearrangement of the low-temperature to the high-temperature form of single crystals of binaphthyl at least under our experimental conditions occurs as a sublimation process rather than as a solid-solid transformation as had been previously proposed.[4] It is of interest in this connection that kinetic studies have given values for the energy of activation for the solid-state rearrangement of polycrystalline samples of racemic to chiral binaphthyl of 58–67 kcal/mol and it had been noted that "the high activation energy and entropy are consistent with a picture in which the molecule of 1,1′-binaphthyl attains a great deal of freedom from the solid, similar to that obtained by transfer to a gas phase...."[4b] The differences in the molecular conformation that would take place as a result of the transformation of a crystal of the low- to the high-temperature form are considered in the following section.

Molecular Geometry. Drawings of the binaphthyl molecules in the A and B forms are shown in Figure 3. The most significant difference is that in the A form, the molecule has a trans arrangement around the central C(1)–C(1′) bond with a dihedral angle of 103.1°, while in the B form, it is cis with a dihedral angle of 68.6°. Bond lengths and angles for the two forms are shown in Figure 4; within the accuracy of the analysis, there are no significant differences. In the A form, both phenyl rings show slight distortions from strict planarity. The best planes through the atoms of the two six-membered rings make an angle of 1.7° with each other. The ring comprising C(1)–C(8A) is slightly more planar than that with C(5)–C(4A). C(1′) lies essentially in the

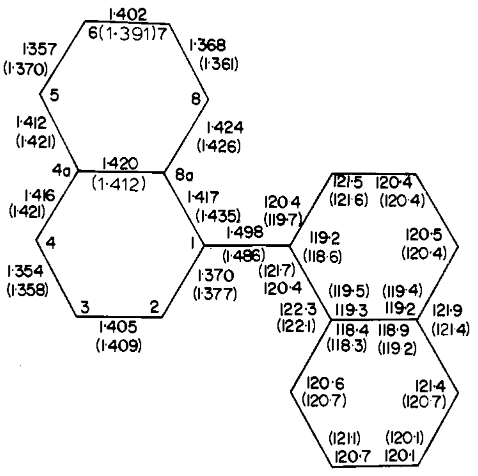

Figure 4. The bond lengths and angles in the A form of binaphthyl compared to those in the B form (parentheses). The esd of the lengths and angles in both forms are 0.003–0.004 Å and 0.2–0.3°.

plane of the naphthalene nucleus of binaphthyl. In the B form, the deviations from planarity are less marked. The two six-membered rings are inclined at an angle of 1.0°; once more the ring not bearing the central C–C bond is slightly less planar than the other, and C(1′) is in the plane of the naphthalene moiety. Details of the best plane calculations are given in Table III.

It would appear that the exact conformation found for the binaphthyl molecule in both crystalline forms is not determined by intramolecular interactions. In the cis form, the shortest H···H contact is of 2.81 Å between H(8) and H(8′) and the C(1)···H(8′) and the C(1)···H(2′) distances are 2.62 and 2.67 Å. In the trans form, the shortest H···H distance is 3.03 Å between H(2) and H(8′) and the C(1)···H(8′) and C(1)···H(2′) distances are 2.59 and 2.65 Å. The H···H contacts are well above twice the van der Waals radius for hydrogen.

Packing. The packing of the cis form is shown in Figure 5. The molecules can be thought of as forming two-dimensional layers normal to the *a* axis. The planes of the naphthalene nuclei and the C(1)–C(1′) peri-bond are all normal to these layers. The H(4) and H(5) hydrogen atoms point out from the layers and into appropriate hollows in the adjacent layers. The shortest interlayer H···H contact is of 2.52 Å between H(5) in the reference molecule and H(4) in the molecule at $^1/_2 - x, -^1/_2 + y, ^1/_2 - z$. Within the layer, the shortest contact is of 2.45 Å between the reference H(8) and H(8) in the molecule at $1 - x, -y, -z$. H(8) and H(7) also have contacts of 2.60 and 2.58 Å, respectively, with H(2) in the molecule at $1 - x, -1 + y, ^1/_2 - z$.

In the trans or chiral form, no such a well-defined layer structure is evident, although "layers" can be chosen in the (012) or (102) planes. Such a "layer" in the 012 plane is shown in Figure 6. Within this "layer" there are a number of relatively short contacts involving C–H bonds that are almost normal to the planes of the aromatic rings. The two hydrogen atoms, H(2) and H(3), of the ring related by symmetry $\bar{y}$, $1 - x, ^1/_2 - z$ lie 2.97 and 2.91 Å, respectively, from the reference naphthyl ring with the shortest atom—atom contact being 2.97 Å between C(8) and H(3). On the other side of the ring, H(5) and H(6) of the ring at $^1/_2 + x, ^1/_2 - y, ^3/_4 - z$ lie 2.58 and 2.86 Å from it with the shortest atom—atom contact being 2.79 Å between C(8A) and H(5). Other short contacts are H(4)···H(3) ($\bar{y}, \bar{x}, ^1/_2 - z$) of 2.61 Å and H(6)···H(8) ($-^1/_2 + x, 1^1/_2 - y, ^3/_4 - z$) of 2.55 Å.

There is a considerable difference in the calculated densities of the two forms, 1.18 g cm^{-3} for the chiral form and 1.28 g cm^{-3} for the racemic form, data that are indicative of a more efficient packing for the molecules as a racemate.

Relationship between the Development of Hemihedral Faces and Miller Indices of Crystal Faces. Wilson and Pincock reported[4a] that one crystallization produced especially large crystals (1–4 mm in length) but that hemihedral faces (indicating enantiomorphic character) could not be observed even though high rotations were obtained when the crystals were dissolved in benzene. Our identification of the crystal faces most commonly developed by our crystals shows them to be (001), (012), and the additional symmetry-related faces $(00\bar{1})$, $(\bar{1}02)$, $(0\bar{1}2)$, (102), $(0\bar{1}\bar{2})$, $(10\bar{2})$, $(01\bar{2})$, and $(\bar{1}0\bar{2})$. It can be seen that the symmetry operations of class 422 require that each face of this set be accompanied by a parallel face at the opposite side of the crystal; there are no hemihedral faces to reveal the chirality of such a crystal.

The question naturally arises what faces, if any, would have given rise to hemihedral faces in a crystal of this class? Application to a general face (*hkl*) of the symmetry operations of class 422 shows that certain requirements must be met if a face is not to be accompanied by a corresponding parallel face $(\bar{h}\bar{k}\bar{l})$. These requirements are as follows: $h \neq k$; $h \neq 0$; $k \neq 0$; $l \neq 0$.

Thus, the lowest order face which would be hemihedral and would not be accompanied by a parallel counterpart is (121).

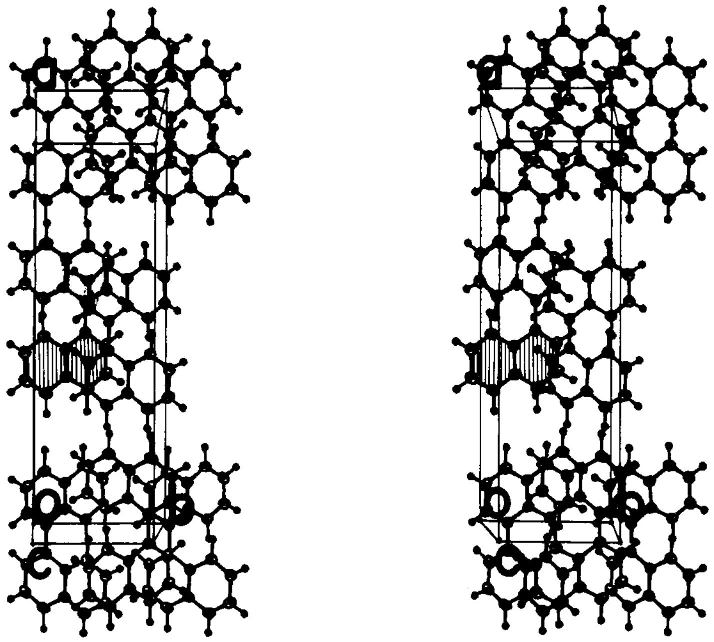

Figure 5. Stereoscopic view of the packing in the crystal of the cis or B form of binaphthyl. The aromatic rings of the reference half-molecule are shaded.

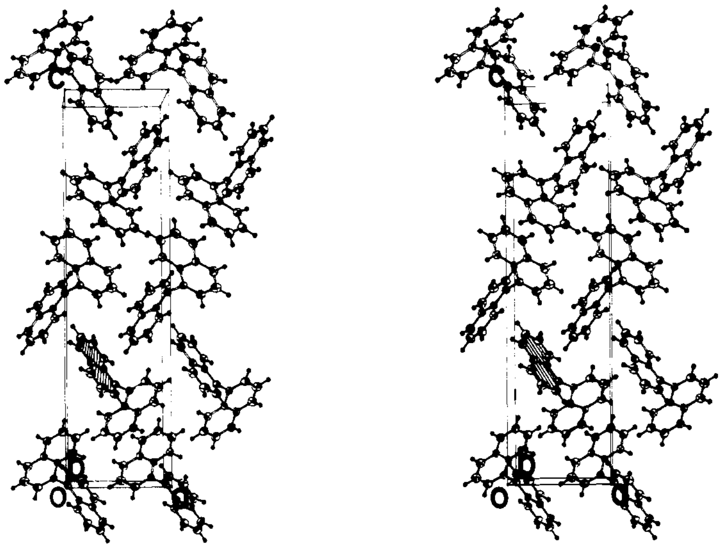

Figure 6. Stereoscopic view of the packing in the crystal of the trans or A form of binaphthyl. The aromatic rings of the reference half-molecule are shaded.

Since higher order faces are less likely to be formed than lower,[10] it is not surprising that hemihedral crystals have not been observed here.

Because crystal class 422 is a rather rare one,[11] it is of interest to apply the above analysis to those classes which contain most chiral organic compounds, *i.e.*, the classes 2 and 222. The twofold rotation axis of class 2 produces from face (hkl) only the face $(\bar{h}k\bar{l})$. Therefore, unless $k = 0$ the twofold symmetry operation does not produce $(\bar{h}\bar{k}\bar{l})$ from (hkl); that is, as long as $k \neq 0$, a face (hkl) will be hemihedral. A classic example is *dl*-tartaric acid which, although its racemate does not crystallize as a conglomerate, when resolved forms enantiomeric crystals with faces of order no higher than (110); yet, the chirality of the (+) and (−) crystals is clearly indicated by the crystal morphology.[12,13]

The most common crystal class for chiral substances is 222.[11] In this case the operation of three mutually perpendicular twofold axes on (hkl) produces $(\bar{h}\bar{k}l)$, $(\bar{h}k\bar{l})$, and $(h\bar{k}\bar{l})$. It follows that if h or k or $l = 0$ the face (hkl) is not hemihedral. In other words to be hemihedral a face must be of order (111) or higher, a more severe requirement than was found in the case of class 2. In addition the orthorhombic crystals of class 222 lack the assistance in orientation provided by the nonorthogonal a and c axes of the monoclinic class 2.

Conclusion. Although our work does not preclude the existence of a solid-state conversion of racemic to chiral 1,1-binaphthyl, it establishes that such a process, under our reaction conditions, is overshadowed by one proceeding by vaporization and recondensation. The solid-state racemization of 4,4′-diamino-1,1′-binaphthyl has been observed to occur with a half-time of about 2 months at room temperature[14] and has been studied in some detail.[15] It has been pointed out that the phase diagrams of the diaminobinaphtyl and of 1,1′-binaphthyl, the subject of the present paper, are qualitatively similar and the fact that one undergoes thermal racemization while the other undergoes the opposite reaction, thermal resolution, is due to the different ranges of temperature in which the two forms are stable. No crystallographic data are available for the diaminobinaphthyl, and a further investigation of such compounds would be of great interest.[16]

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Supplementary Material Available: Final thermal parameters and the lists of structure factors for the structures of both forms of binaphthyl (19 pages). Ordering information is given on any current masthead page.

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(10) P. Hartman, "Physics and Chemistry of the Solid State", Vol. 1, D. Fox, M. M. Labes, and A. Weissberger, Eds., Interscience, New York, 1963, p 377.

(11) V. K. Belsky and P. M. Zorkii, *Acta Crystallog., Sect. A*, A33, 1004 (1977); A. D. Mighell, H. M. Ondik, and B. B. Molino, *J. Phys. Chem. Ref. Data*, 6, 675 (1977).

(12) See I. C. Paul and D. Y. Curtin, *Science* (*Washington, D.C.*) **187**, 19 (1975) for stereopair drawings of left- and right-handed tartaric crystals.

(13) The remarkable confluence of favorable circumstances which made possible the mechanical resolution of sodium ammonium tartrate tetrahydrate by Pasteur has been pointed out.[5] Since this salt crystallizes in class 222 there must be added the other fortunate coincidence: the development of the (111) face (and its symmetry-generated relatives) on crystallization of this salt which made possible the visual distinction between the (+) and (−) crystals.

(14) W. Theilacker and R. Hopp, *Chem. Ber.*, **92**, 2293 (1959).

(15) M. D.-M. Lu and R. E. Pincock, *J. Org. Chem.*, **43**, 601 (1978).

(16) After submission of this manuscript, we learned that Professor J. Trotter of the University of British Columbia had determined the structure of the chiral form of binaphthyl in addition to the determination of a racemic and chiral form of 4,4′-dimethylbinaphthyl. After acceptance of the paper and while the results of this paper were being described at the J. M. Robertson 80th Birthday Symposium at Glasgow Scotland, we learned that R. Kuroda and S. F. Mason (Kings College, London) had also determined the structure of the chiral form of binaphthyl and had a paper in press (*J. Chem. Soc.*).