Thermally Induced Resolution of Racemic 1,1'-Binaphthyl in the Solid State

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Abstract: The development of optical activity in racemic samples of 1,1'-binaphthyl can occur simply on heating polycrystalline samples at 76–150°. This unusual solid-state resolution is made possible by a phase transformation from a racemic compound (mp 145°) to an unequal eutectic mixture (mp 158°) of enantiomorphic crystals, with the necessary enantiomer conversion occurring in the reactant–product interface. The extent of this resolution in the solid state is very sensitive to the previous history of samples, i.e., to inadvertent seeding, to crystal size or extent of grinding of crystals, and even to storage time of samples (at 0 or 25°). However, polycrystalline 1,1'-binaphthyl samples having very low optical activity and having the correct phase content and distribution for conversion to highly resolved material can be easily and reproducibly prepared. At 150°, these samples resolve via a racemate → melt → eutectic phase transition, from $[\alpha]D$ 1–10° to $[\alpha]D$ >200° in the desired positive or negative direction within a few minutes. This corresponds to more than 81% optical purity. Below 145° and above 76°, samples from these special preparations convert in a kinetically smooth manner to optically active binaphthyl. In this temperature range, as shown by the phase diagram of the 1,1'-binaphthyl system, the conversion occurs entirely in the solid state.

The general potential of the solid state for new types of reactions, with high yields and stereospecificity, has long been recognized. Nevertheless, relative to often highly developed studies of reactions in solutions, organic reactions in the solid state have received little of their deserved attention.[1] In the solid state, problems with reproducibility commonly arise as a result of sensitivity to impurities, lattice defects, dislocations, size of crystals, and other hard-to-control variables related to the preparation of samples. Organic chemists, at least, have tended to avoid such problems by using solution reactions.

In spite of these general difficulties, the solid state presents one greatly redeeming aspect: the possibility of extremely selective stereochemical control by the crystal lattice. Specifically, when a chemical reaction yielding two or more products occurs in the solid state, the high degree of organization in either the reactant lattice or the product lattice can bring about a steric selection from among the possible products. There are many examples of this stereospecificity, with both photochemically[1a] and thermally induced reactions,[1b] but they almost exclusively illustrate *reactant-lattice control* by the diminishing reactant crystals on the evolving products. For example,[2] a most striking case involves the interaction of bromine vapor with a single crystal of 4,4'-dimethylchalcone, an achiral compound which, however, crystallizes in an enantiomorphic space group. The resulting addition product was obtained with one enantiomer in slight excess. In this case of absolute asymmetric synthesis,[3] the stereospecific yields, while significant, are rather low. This result may be due either to poor reactant-lattice control or else to the increasing disorganization of the reactant lattice itself as the product develops. On the other hand, an example of *product-lattice control* would not suffer from the major disadvantage of progressive lattice destruction. On the contrary, the product lattice, once formed, remains intact. Steric control may then be efficiently maintained at the growing crystal surface during the complete conversion to products. Such a "feedback mechanism"[1a] could greatly amplify an initial steric choice and therefore lead to high stereospecificity in the product.

The transformation of solid, racemic 1,1'-binaphthyl into one of its enantiomers is a case of absolute asymmetric synthesis where stereochemical control by product crystals is possible,[4] and we report here our results for the solid-state to solid-state resolution. The spontaneous resolution of 1,1'-binaphthyl by crystallization from supercooled melts, i.e., a liquid-state to solid-state resolution has previously been described in detail.[5,6]

Classical Resolutions of 1,1'-Binaphthyl

The compound 1,1'-binaphthyl is one of the simplest chiral hydrocarbons. Its dissymmetry is molecular in nature, and enantiomer interconversion is possible simply by rotation about the interannular bond rather than by any bond-breaking process.

$(R)-(-)-1,1'$-binaphthyl $(S)-(+)-1,1'$-binaphthyl
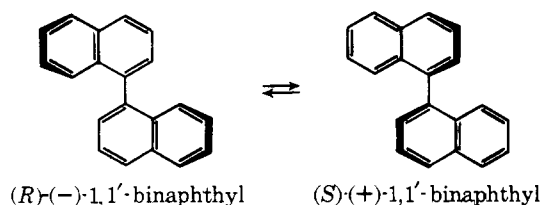
Two crystalline forms of binaphthyl (mp 145 and 158°) have been noted.[7] The low-melting form, mp 145°, is known from X-ray structural analysis[8] to belong to a centrosymmetric space group with a unit cell consisting of two molecules having R configuration and two having S configuration; i.e., the low-melting form is a racemic compound (racemate) and is, of course, optically inactive.

Optically active binaphthyl was first synthesized in 1963 by deamination of its 4,4'-diamino derivative which had been resolved through use of the resolving agent α-bromo-π-camphorsulfonic acid.[9,10] The highest rotation of binaphthyl obtained by this method was $[\alpha]D$ +192°.[11,12] S-(+)-1,1'-Binaphthyl has a half-life for racemization in several solvents of ca. 10 hr at 25°;[9,12] the rotation around the interannular bond is sufficiently restricted to allow both the isolation of enantiomers and the measurement of optical activities in solution at room temperature before appreciable racemization occurs.

Optically active binaphthyl can also be obtained in small quantities by the oldest method of resolving racemic materials, i.e., hand picking of single crystals.[13] Among many crystallizations of binaphthyl, one happened to form especially large crystals (ca. 1–4 mm in length from acetone at room temperature over several days). Hemihedral faces (indicating enantiomorphic character) were not sufficiently well developed to be observed;[14] however, single crystals gave high rotations when dissolved in benzene. Ten well-

formed crystals, picked at random, gave the following specific rotations: $[\alpha]$D +222, +208, +203, +207, −199, +212, −164, −204, +222, +197° (crystal weights from 2.45 to 11.30 mg). Such single crystals were shown by infrared analysis[7] to be the high-melting form and, since they consisted of highly resolved binaphthyl, the high-melting (158°) form is a eutectic mixture of individual R and S crystals rather than a solid solution or a second racemate. This form does not show the characteristic eutectic liquidus curve, with resolved binaphthyl melting higher than the racemic material, because of the rapid interconversion of R and S conformational enantiomers in the melt at 158° ($t_{1/2}$ = ca. 0.5 sec at 160°). Rather, all samples of this eutectic form, of any optical purity, are observed to melt at 158°, which is the eutectic temperature of the system.

Phase Diagram of the 1,1'-Binaphthyl System

To understand the conversions of the three forms of binaphthyl (low melting = L, high melting = H, and melt = M) and the associated development of optical activity, the relative stabilities of these forms at various temperatures must be known; i.e., the phase diagram must be established. From the easily observed phase transitions (L → M at 145°, H → M at 158°), two free-energy situations are possible as shown in Figure 1. Either the eutectic form H is the more stable (has lower energy as shown in Figure 1a) at all temperatures up to the melting point at 158°, or an equilibrium solid–solid phase transition point τ exists (as shown in Figure 1b) below which the racemate L is the more stable form. The corresponding phase diagrams are shown in Figures 1c and 1d, respectively. In order to determine which phase diagram is the appropriate one, interconversions of the two solid forms from room temperature to 145° were investigated by long-term heating of samples, by solution-phase transformations[15] (i.e., L → solution → H and H → solution → L), by differential scanning calorimetry,[16] and by thermodynamic calculations. The conversions L → H and H → L in solid binaphthyl did not noticeably proceed at room temperature, even when solution-phase transformations, which can greatly speed up phase changes,[15] were attempted. However, the transition L → H was observed to occur in neat samples of binaphthyl heated at higher temperatures, from 145° down to as low as 76° (where 10% conversion was detected after 26 weeks). An upper limit of 76° for any solid–solid transition point (τ in Figures 1b and 1d) is thereby established. In addition, the heats of melting of low- and high-melting forms (7.29 ± 0.15 and 5.67 ± 0.08 kcal mol⁻¹, respectively) and the heat-capacity difference of these two forms (13 ± 4 cal deg⁻¹ mol⁻¹), all measured by differential scanning calorimetry, were used to calculate an approximate L ⇌ H transition temperature in the region of 86°.[17a]

Circumstantial evidence that the racemate form is more stable at room temperature (i.e., $\tau > 25°$) is available from the fact that slow evaporation over several days of a racemic binaphthyl solution in ether, acetone, or benzene at 25° gives racemate with very little eutectic form, while rapid evaporation in less than 5 min in a stream of dry air at 25° gives eutectic form largely free from racemate (by X-ray powder analysis). Similarly, slow and rapid cooling of small samples of melted binaphthyl on the scanning calorimeter give pure racemate and pure eutectic form, respectively. If it is true, as suggested,[15] that a more supersaturated solution or a more supercooled melt usually produces the less stable crystal form, then the racemate is more stable at room temperature.

The binaphthyl phase relationship is therefore the one shown in Figure 1d and has the following features: (1) rela-
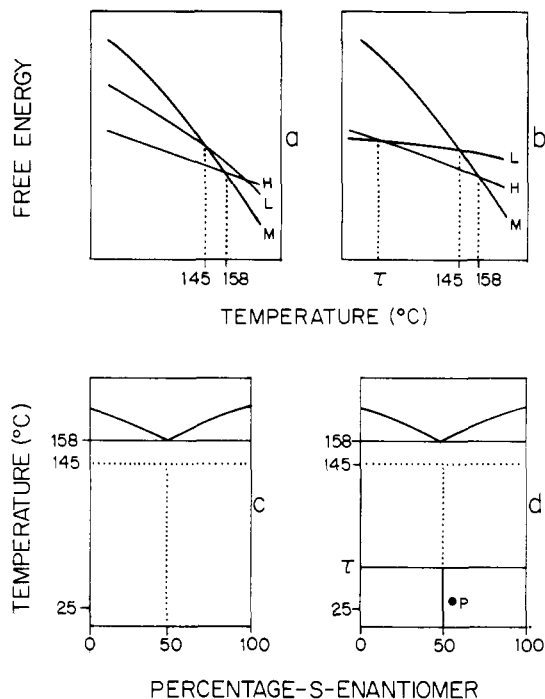

Figure 1. (a and b) Schematic plots for two possible free energy-temperature relationships of the forms of racemic 1,1'-binaphthyl; low-melting form = L, high-melting form = H, and melt = M. (c) Phase diagram which corresponds to a. (d) Phase diagram which corresponds to b.

tively rapid heating of racemate form (in the metastable state indicated by the vertical dotted line) results in melting at 145° and recrystallization to eutectic form (mp 158°) which may be optically active; and (2) from $\tau = \sim76$–145°, the racemate form is unstable relative to separate crystals of (R)- and (S)-binaphthyl, and therefore slow solid-state transformation to optically active material is possible. The existence of the phase relationship in Figure 1d rather than the relationship in Figure 1c suggested the finally successful means (see below) of preparing samples of binapthyl which resolve smoothly from essentially inactive material to $[\alpha]$D ca. ±200° on heating.

The Behavior of Solid Racemic 1,1'-Binaphthyl

During the course of this study, many preparations of racemic binaphthyl were carried out. These were produced from 1-bromonaphthalene via copper(II) chloride promoted coupling of the corresponding Grignard reagent.[18] Since chiral agents were absent during the preparations, "racemic"[19] product was guaranteed. However, the heating at 120–150° of small samples (ca. 20 mg) of polycrystalline binaphthyl taken from different racemic preparations surprisingly produced optically active material (in 11 out of 14 preparations). Furthermore, within a given preparation, the rotations produced were all of the same sign (all positive in six preparations, all negative in five preparations), although completely scattered with respect to heating time (see Figure 2). Since both (R)- and (S)-binaphthyl had been produced in our laboratory before the racemic preparations were carried out, it is possible that trace quantities of one of the enantiomers may have existed in each of the preparations, thereby influencing the crystallization of eutectic form at higher temperatures. In any case, other than a consistency of either positive or negative rotations, there is no control over the resolution in ordinarily prepared racemic samples of binaphthyl.

By taking advantage of the above observations, highly re-
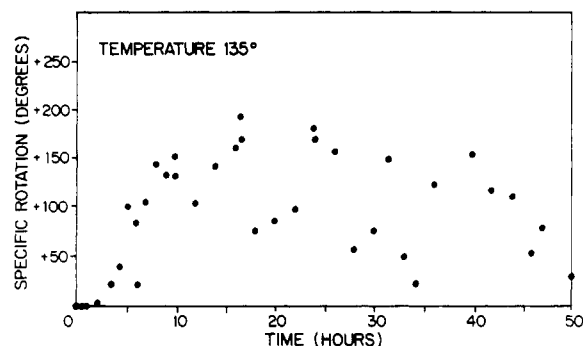
Figure 2. Specific rotations produced at 135° in polycrystalline samples of 1,1'-binaphthyl taken from an ordinarily prepared racemic sample.

Figure 3. Specific rotations produced at 125° in polycrystalline samples of 1,1'-binaphthyl taken from a specially prepared near-racemic sample.

solved binaphthyl may be obtained from racemic material by a series of heating, crystallizing, and heating cycles[4] (see Experimental Section). Each cycle produces an increment in optical activity which, although unpredictable in magnitude, eventually leads to high optical purities. This method is convenient for producing larger quantities of resolved binaphthyl without the necessity to resort to resolving agents and multiple chemical transformations as in the classical resolution procedure. However, the most desirable way of obtaining resolved binaphthyl would be simply to go from some form of racemic binaphthyl to highly resolved material in one step, and such a method was actively sought.

Resolution of Artificially Seeded Binaphthyl

Many experiments in which a racemic preparation was intentionally seeded with small amounts of highly resolved binaphthyl were carried out. The simplest experiments were the physical addition of highly optically active seed crystals to liquid-phase racemic binaphthyl at temperatures where the interconversion of enantiomers was very rapid. The liquid phase was either the supercooled melt at 135-150° or else a supersaturated solution at 120 (in 1-propanol, sealed tube) or 140° (in ethylene glycol). Although some experiments gave binaphthyl having a specific rotation greater than 200°, attempts to reproduce these successful resolutions usually failed. These failures probably reflect the difficulty in distributing seed crystals extensively in a racemic material and also the difficulty in preventing inadvertent seeding by an unwanted enantiomeric form.[20]

An interesting alternative procedure, which eventually led to a method of consistently producing highly resolved binaphthyl in one step, was derived from an examination of the phase diagram (Figure 1d). Point P on the diagram represents a sample of binaphthyl at 25° with a low optical activity, such as [α]D +2. Because the binaphthyl system has the phase relationship as in Figure 1d rather than Figure 1c, the *stable* state at 25° would consist *only* of small amounts of (S)-(+) crystallites distributed among racemate crystals. At equilibrium, no (R)-(−) crystal can be present. If such a thermodynamically stable two-phase mixture could be prepared, and provided that no spontaneous nucleation of (R)-(−) form occurs, then the simple heating of samples above the transition point τ would result in effective control by (S)-(+) crystals over the ensuing conversion of the racemate form to eutectic form. The entire sample would then resolve to (S)-(+)-binaphthyl in a drive toward lower free energy. Two types of resolutions can be distinguished on the basis of whether or not the melt is involved: in the temperature range 76-145°, a racemate → eutectic transformation occurs (i.e., only the two solid states, reacting crystals and product crystals, are present), whereas
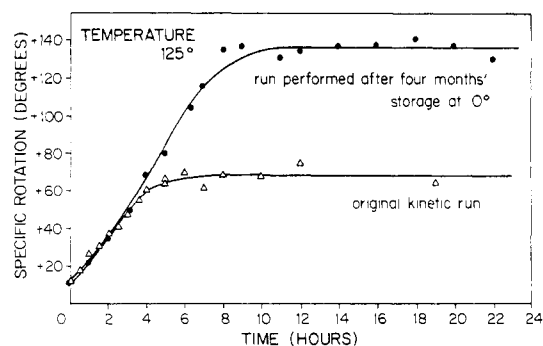
from 145 to 158°, a racemate → melt → eutectic transformation takes place (i.e., the melt is an intermediate state).

The most stable state near room temperature might best be attained by slow evaporation of a solvent and growth of crystals under near-equilibrium conditions. However, samples prepared by this simple procedure gave inconsistent results on heating, and a number of variations in crystallization parameters, such as nature of solvent, concentration and activity of binaphthyl, temperature, and rate of crystallization, made little difference. Finally, one technique gave excellent results. The method[21] involves dissolving 1,1'-binaphthyl, [α]D ±2-15°, in acetone, filtering the solution, and then cooling with swirling at −78° until crystals appear. The flask is transferred to a bath at 20-25° and evaporated in a rotary evaporator. Most (but not all) of the crystals dissolve as the solution warms; thereafter more crystals separate as the loss of solvent continues (recovery is 100% after ca. 30 min). These product crystals, in 15 out of 16 independent preparations, resolved very well; they gave specific rotations of at least ±190° (78% optically pure) in the chosen direction on heating at 150° in a racemate → melt → eutectic transformation.

In samples taken from these special preparations, and in great contrast to the type of results shown in Figure 2, smooth development of optical activity occurred in the racemate → eutectic solid-state transformation. Figure 3 shows the development of specific rotations in samples taken from a binaphthyl preparation with initial [α]D +11.8°. This binaphthyl resolves within 1 min to +226° (92% optical purity) on heating at 150° but, as shown, gives only [α]D +60° in the solid-state resolution at 125°. Samples change on storage; after 4 months at 0°, this material gave a final [α]D +140° when heated at 125° (see Figure 3). Table I gives the final rotations attained in several special preparations of this near-racemic material at various temperatures. High rotations were achieved in all cases at 150° in the racemate → melt → eutectic transformation, while lower rotations were sometimes obtained below 145° in the direct racemate → eutectic solid-state reaction. This may reflect some spontaneous nucleation of undesired enantiomer in the longer times required to carry out the solid-state reaction at 76-145°. As shown in Table I, the rate and extent of resolution still depends on detailed aspects of the past history of samples such as storage times, particle size, or extent of grinding of samples. However, the ability to produce quantities of smoothly resolving polycrystalline binaphthyl will allow a more thorough kinetic analysis of this solid-solid transformation.

Summary

The development of optical activity simply by heating a racemic material like 1,1'-binaphthyl may seem, at first

Table I. Final Specific Rotations Obtained from Specially Prepared Samples of 1,1'-Binaphthyl at Various Temperatures

Preparation no.	Temp, °C	Final $[\alpha]D^{25}$	Time to attain final $[\alpha]D^{25}$
S-1[a]	150	+211	<50 min
	135	+201	80 min
	135[b]	+201	100 min
	135[c]	+182	30 min
	135[d]	+61	6 min
	105	+221	288 hr
	98	+227	4180 hr
S-2	150	+226	<1 min
	135	+84	35 min
	125	+67	5 hr
	125[e]	+136	8 hr
	115	+110	50 hr
	105	+123	288 hr
S-3	150	+200	<1 min
	135	+201	12 min
	125	+214	38 min
	115	+223	12 hr
	105	+229	96 hr
	93[d]	(+125)[f]	(670 hr)[f]
	87[d]	(+77)[f]	(670 hr)[f]
	83[d]	(+26)[f]	(670 hr)[f]
	76[d]	(+11)[f]	(670 hr)[f]
	76[d]	(+22)[f]	(4280 hr)[f]
	64[d]	(0)[f]	(4280 hr)[f]
R-1	150	−233	<1 min
	135	−123	30 min
	125	−71	300 min
	115	−69	30 hr
	105	−79	192 hr

[a] Initial rotations of individual preparations were: S-1, +1.4; S-2, +11.8; S-3, +1.8; R-1, −11.0°. [b] Run performed after 6 weeks of storage at 25°. [c] Run using ground samples. [d] Run using more highly ground samples. [e] Run performed after 4 months of storage at 0°. [f] Final rotation not established.

thought, to be an impossible process. The thought arises because the interconversion of enantiomers in solution always leads to racemization rather than resolution. But in contrast to a homogeneous system, a heterogeneous system, such as the combinations of phases formed between two enantiomers, may favor resolution. Resolution in the 1,1'-binaphthyl system occurs since the phase transition from racemate to eutectic form lowers the free energy of the system, a process which more than compensates for the free-energy increase when molecules of one kind are formed from an equally populated (R)-(−) and (S)-(+) system.

The fact that an entire sample of virtually racemic binaphthyl can convert to essentially one enantiomer means, of course, that enantiomer conversion must occur in the sample. At 150°, where the racemate melts and leaves behind any seed crystal of resolved eutectic form, racemization occurs very rapidly in the melt ($t_{1/2} = 0.5$ sec). Growing (S)-(+) crystals, for example, can select S molecules from a melt which is essentially always racemic until it is finally converted completely into solid S enantiomorph. In the temperature range of ~76–145° where the sample is entirely solid, enantiomer interconversion (which is only a simple conformational change) most probably occurs in the highly disorganized interface between growing S crystals and disappearing racemate crystals.

The liquid → solid resolution of binaphthyl can be carried out under conditions where the production of one enantiomorph is intrinsically spontaneous,[5,6] but the solid → solid resolution of racemic material is very sensitive to the presence of adventitious seeds and, as a result, very erratic in its resolution behavior. However, a smooth development of optical activity, with high stereospecificity, can be consistently achieved simply by heating specially prepared near-

racemic binaphthyl samples. Although a considerable degree of reproducibility and stereospecific control has therefore been attained, separate batches of binaphthyl do retain individual characteristics such as various rates and degrees of resolution.

Experimental Section

Preparations. Racemic naphthidine (4,4'-diamino-1,1'-binaphthyl) was prepared in 26% yield from 1-aminonaphthalene by the method of Cohen and Oesper;[22] it was resolved by crystallization of its α-bromo-D-camphor-π-sulfonate salt[23] and deaminated to (S)-(+)-1,1'-binaphthyl, $[\alpha]D^{25}$ +97°, mp 156–157° [lit.[9,10] $[\alpha]D^{25}$ +145–192°, mp 156–159°]. This classical resolution method is workable but very time consuming and inefficient in comparison to resolutions described below.

Racemic 1,1'-binaphthyl was prepared from 1-bromonaphthylene[18] and the crude product purified by chromatography on alumina (12 g on 300 g) through elution with 3 l. of 10% benzene-petroleum ether (30–60°). The two crystal forms of 1,1'-binaphthyl were characterized by their different infrared spectra (in Nujol mulls),[7] by X-ray powder diffraction patterns, and by differential scanning calorimetry (a Perkin-Elmer Model DSC-1B was used).

The high-melting form of binaphthyl can be obtained uncontaminated with low-melting form simply by heating any sample of binaphthyl at 145–158°. Workable quantities of the low-melting form are difficult to obtain completely free from seeds of high-melting form, but the best samples are available by slow evaporation and accompanying crystallization (over several days at room temperature) of filtered solutions of racemic binaphthyl in ether, acetone, or benzene.

Pure low-melting form could be obtained, however, in small quantities (<5 mg) using the differential scanning calorimeter. When pure binaphthyl, regardless of its phase content or activity, was melted above 160°, then program cooled (at rates up to 20 deg min⁻¹) to 50–60°, the sample solidified. On reheating at any programming rate, only the racemate endotherm was observed, and no eutectic form crystallized from the melt above 145° (i.e., no eutectic seed crystals were present). In contrast, if the same sample was melted above 160° and cooled very quickly by removing the sample planchette and placing it on a metal surface at room temperature, a glass formed; if the sample was replaced in the holder then reheated, it solidified at about 90–100°, then melted at 157–158°, with no indication of any low-melting form. This micro (5 mg) method of preparing the pure high- and low-melting forms is surprisingly reproducible; the same sample can be converted back and forth indefinitely to either form, simply by varying the rate of cooling. Attempts to scale up greatly the size of the sample were unsuccessful.

Resolutions. A. By Heating, Cooling, and Crystallizing Cycles. Racemic 1,1-binaphthyl, 2.0 g, in a sealed ampule was immersed in a 150° bath for 2 hr (the sample appeared to remain solid throughout), then cooled to room temperature. Polarimetric analysis of a small portion of the sample gave $[\alpha]D$ +42. The sample was dissolved in 400 ml of pentane, and the solution was filtered, boiled down to 150 ml, allowed to cool to room temperature (total time at the boiling point of pentane was 15–20 min), and held at 0° for 1 hr. The pentane was removed on a rotary evaporator to give quantitative yields of material having specific rotation of +43°. The binaphthyl was then sealed in a second ampule and heated, as before, at 150° for 2 hr. The product had $[\alpha]D$ +115°. Recrystallization from pentane was repeated in exactly the same manner as before, preparing the material for the third heating at 150° (after which a specific rotation of +185° was observed). The cycle was repeated a fourth time to obtain 1.10 g (the weight losses due mainly to samples taken for polarimetric and differential scanning analyses) of (S)-(+)-1,1'-binaphthyl, $[\alpha]D$ +194°. Another series of cycling experiments gave resolved binaphthyl in the following progression: $[\alpha]D$ 0, −50, −79, and −194° in three cycles.

Multiple recrystallizations of a well-resolved sample of binaphthyl gave material with the highest observable rotation. For example, starting with 1.53 g of binaphthyl, $[\alpha]D$ −216°, in 180 ml of acetone, 0.5 g of binaphthyl having $[\alpha]D$ −245 ± 1° was obtained after four recrystallizations between room temperature and −78°. Further recrystallization did not increase the rotation. Because of the slow interconversion of enantiomers in solution and because the

resolution by crystallization may be limited by the presence of a solid solution with a few per cent of one enantiomer in the other, the $[\alpha]D \pm 245°$ represents the practical maximum observable rotation.

B. By Heating Near-Racemic Samples. Binaphthyl that resolved to at least $[\alpha]D \pm 190°$ (78% optical purity) on heating to 150° for 2 hr and which gave a smooth development of optical activity at lower temperatures was prepared by the following procedure. For example, a solution of 0.133 g of active 1,1'-binaphthyl ($[\alpha]D$ +92°) and 5.57 g of racemic 1,1'-binaphthyl (comprising together 5.70 g of material with $[\alpha]D$ +2.2°) in 400 ml of acetone was filtered into a 1-l. round-bottom flask. The solution was then cooled in a Dry Ice–acetone bath (−78°) for 10 min with swirling, during which time crystallization began. Without completing the crystallization, the flask was removed from the cold bath and immediately placed on a rotary evaporator. The flask was rotated while full vacuum (water aspirator) was being established, then lowered into a water bath maintained between 20 and 25°, and the rotation was continued. As the flask warmed, some (but not all) of the crystals dissolved, then reprecipitation began with the loss of solvent. The evporation was taken to dryness, with any residual acetone removed at room temperature with a vacuum pump. The finely crystalline binaphthyl, which was 100% recovered, possessed an activity of $[\alpha]D$ +1.8°, and resolved to >+200° on heating at any temperature between 105 and 150°.

Polarimetry. To analyze the development of optical activity in any preparation of binaphthyl, several 10–30-mg samples of the neat, polycrystalline material were sealed in 1-ml ampules. After immersion in a constant temperature bath, individual samples were withdrawn and cooled to room temperature. The solid sample was completely dissolved in benzene, transferred to a 3-ml volumetric flask, and diluted to the mark. Three optical rotation readings (Bendix type 143A Automatic Polarimeter) were made by filling the polarimeter cell successively with three samplings (ca. 0.8 ml each) of the solution. All measurements were made at the sodium D line (5890 Å), and specific rotations were calculated from $[\alpha]D$ $3 \times 10^4 \alpha k$/(sample weight in milligrams) where α is the observed rotation, and k is a cell constant obtained by calibration with known standard sucrose solutions.

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(14) Although enantiomorphic faces can be present in crystals of *R* and *S* enantiomers, they are not easily observable in most cases; see ref 3a.

(15) W. C. McCrone in "Physics and Chemistry of the Organic Solid State," Vol. II, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience, New York, N.Y., 1965, pp 747–753.

(16) Apart from the observation of melting endotherms at 145 and 158°, differential scanning calorimetry was useful in indicating the presence of very small amounts of high-melting binaphthyl in the low-melting racemate: the endotherm at 145° was followed by exothermic crystallization at ca. 150° and finally endothermic melting at 158°. Exothermic crystallization of high-melting form from the melt does not occur at 150° unless a few seed crystals of this form are present originally. At lower temperatures, because of the slow rate of phase changes, differential scanning calorimetry failed to show any other transition points.

(17) (a) For details of this calculation, see K. R. Wilson, Ph.D. thesis, The University of British Columbia, 1972, Appendix B; (b) ibid., pp 100–102.

(18) E. Sakellarios and T. Kyrimis, *Chem. Ber.*, **57**, 324 (1924).

(19) Although optical activity may not be measurable, statistical fluctuations and associated nucleation of predominately one enantiomer during crystallization make it improbable that a solid sample of any "racemic" material has optical activity of absolutely zero. In the case of racemic binaphthyl used here, rotations were zero within the measurable $[\alpha]D$ of $\pm 1°$.

(20) Binaphthyl samples which are completely free from inadvertent seeding can only be obtained by supercooling completely melted samples (previously heated to above 160°) in sealed vials. Such samples give a distribution of rotations that show the generation of optical activity to be absolutely spontaneous.[5,6]

(21) The success of this procedure in eliminating seed crystals of unwanted enantiomer (i.e., in arriving at point P in Figure 1d) may be explained as follows. The initial crystallization at −78° probably brings out all possible solid binaphthyl phases, i.e., (*S*)-(+) crystals, racemate crystals, and (*R*)-(−) crystals. On warming to 20–25°, the (*R*)-(−) crystals (in this example, the undesired enantiomer) dissolve first, leaving only (*S*)-(+) crystals and racemate crystals to induce the precipitation of their own kind. The thermodynamically stable phase mixture at 25° is thereby attained. This is supported[17b] by a consideration of the possible ternary phase diagrams between (*R*)-(−)-binaphthyl, (*S*)-(+)-binaphthyl, and solvent at −78 and 25°.

(22) S. Cohen and R. E. Oesper, *Ind. Eng. Chem.*, **8**, 306 (1936).

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