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Racemic Cis-π-Camphanic Acid. Unusual Solid State Transformation of a Conglomerate into a Plastic Phase

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The phase diagram between the enantiomers of cis-π-camphanic acid has been reexamined by differential scanning calorimetry (DSC). The phase diagram is that of a conglomerate (a mechanical mixture of the crystals of the enantiomers) which transforms into a plastic phase before melting. Despite anomalous thermograms observed on first heating, the existence of a solid solution intermediate between the conglomerate and the plastic phase is not confirmed. At the transition, both an orientational disorder and a molecular diffusion (leading to a chiral disorder) take place. These features are in agreement with the X-ray structure (space group $P6_1$) of the low-temperature form of the enantiomer. This structure suggests an hexagonal compact stacking for the plastic phase.

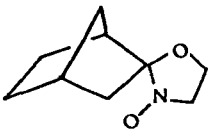
I. INTRODUCTION

As part of a study of molecular racemic crystals undergoing phase transformations in the solid state, we have recently reported that the racemic nitroxide **1** crystallizes as a conglomerate (a mechanical mixture of crystals of the two enantiomers D and L), stable at room temperature, and as a solid solution of enantiomers, stable at higher

temperatures (above ca. 330K).[1] At room temperature, the isothermal transformation of the solid solution (quenched crystal) into the conglomerate, which implies a segregation of the enantiomers in the solid state, was also studied in detail by X-ray analysis as a function of time.

To our knowledge, such a transformation is very unusual. In view of previously reported data,[2,3] we suspected that racemic cis-π-camphanic acid ((±)-2) could exhibit the same behavior. It was claimed that the conglomerate (stable at room temperature) was transformed on heating into a solid solution at 443 K then into a plastic crystal at 481 K eventually melting at 503 K.

In this paper, we report the crystal structure of the enantiomer (−)-2 and new thermal data showing that the melting phase diagram previously published is not correct. In particular, we have been unable to detect any solid solution between the enantiomers.



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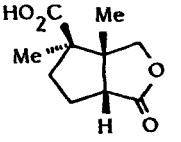

(-)-2

II. PHASE DIAGRAM

The D-L phase diagram (Figure 1) was established by differential scanning calorimetry (DSC) (Perkin Elmer DSC-2C microcalorimeter, sample weights 1–2 mg, heating/cooling rates 10 K.min^{-1}). Several heating-cooling cycles were performed on each sample. (±)- and (−)-2 were recrystallized 2–4 times from MeOH. Some of these samples were further sublimed at 150–160°C under reduced pressure (0.5 mm Hg). Mixtures of (±)- and (−)-2 of known enantiomeric excess were thoroughly ground either directly or after dissolution in a small amount of MeOH followed by evaporation of the solvent.

Within the entire composition range, the melting point was 505 K (ΔH 1.2 ± 0.1 kcal.mol^{-1}) for the first heating run (subsequent runs tend to slightly lower these values presumably due to some degradation upon heating). On cooling, this transition appeared in the range 493–500 K depending on the cooling rate. These features are

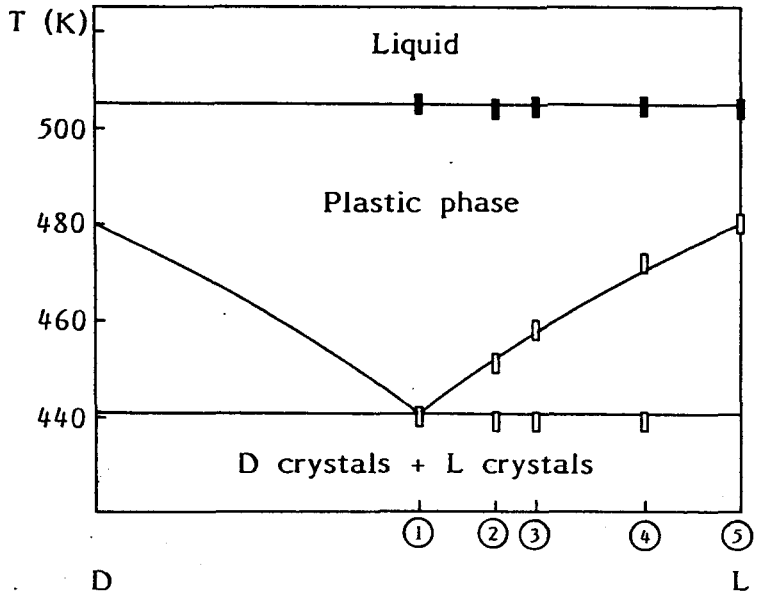

FIGURE 1 Phase diagram of enantiomer mixtures of cis-π-camphanic acid. Experimental points (thermograms 1–5 shown in Figure 2, ■ first heating run, □ second heating run) and calculated curve (the conglomerate curve was calculated from ΔH 7.4 kcal.mol^{-1} and T 480 K, the typical values obtained for the enantiomer transition in the second heating run).

consistent with a plastic crystal-melt transition and with a complete miscibility of the two enantiomers in the plastic state.

An additional transition was observed at lower temperatures whose values depend on the enantiomeric composition. For the pure enantiomer, a sharp peak was found at 481 ± 2 K (ΔH 7.6 ± 0.2 kcal.mol^{-1}) in all heating runs (as above, these values are slightly decreased at each run). In contrast, the racemate purified by recrystallization from MeOH and mixtures prepared from (±)- and (−)-2 samples purified in the same way showed anomalous behavior in the first heating run (Figure 2, on the left). Even using finely ground samples and low heating rates, we always obtained a broad signal with two maxima at ca. 445 and 483 K whose heights were not reproducible from one sample to another. In all subsequent heating runs, the DSC traces (Figure 2, on the right) were perfectly consistent with a conglomerate diagram; in particular, the racemate gave a single peak at 440 K (ΔH 6.6 ± 0.1 kcal.mol^{-1}). When (±)- and (−)-2 were purified by sublimation, the first heating thermograms never

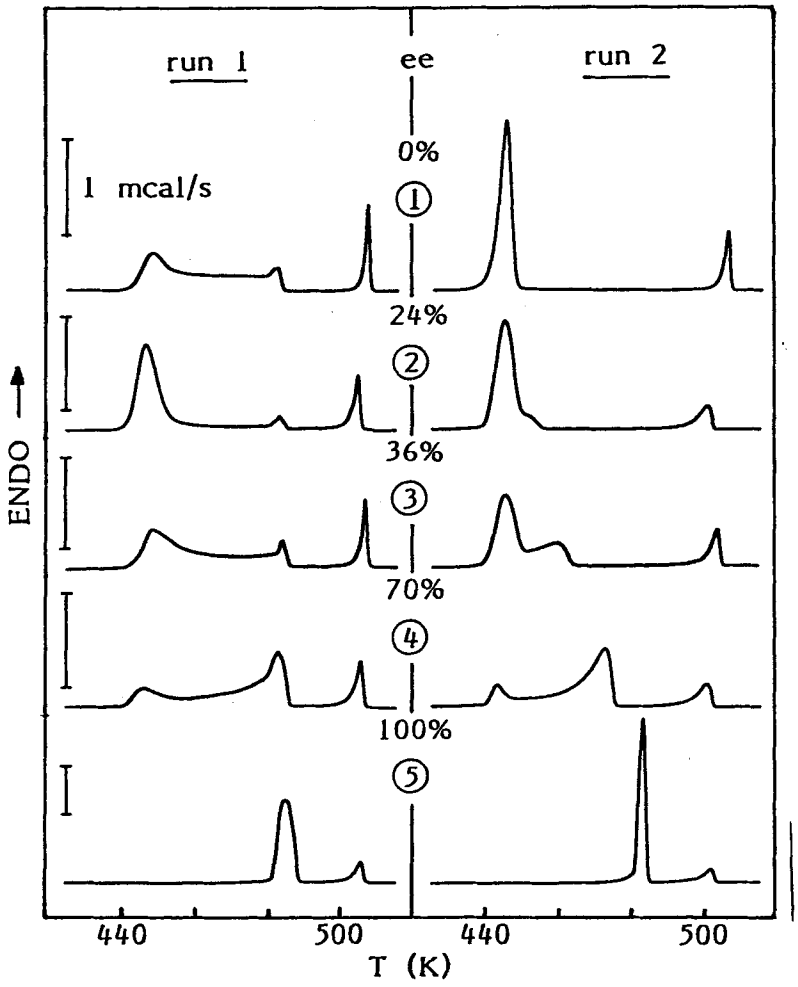

FIGURE 2 DSC thermograms for different enantiomeric compositions (ee) (first and second heating runs).

showed any anomalous behavior and were identical to run 2 in Figure 2 [(racemate transition at 442 K (ΔH 6.8 ± 0.1 kcal.mol^{-1})]. It should be noted that the experimental points in run 2 match the curve calculated by means of Schröder-Van Laar equation.[2] This provides further evidence that, in the plastic phase, the enantiomers are completely miscible with a quasi ideal behavior.

On cooling, the plastic crystal → crystal transition presented undercooling (ca. 40–70 K). A small exotherm was observed in most

of the samples before crystallization. In cases where recrystallization did not occur too rapidly (for enantiomeric excess <25%), this transition was also found upon heating in the same temperature range, 400 ± 5 K (ΔH 0.4–0.6 kcal.mol^{-1}). It would certainly be difficult to determine the exact nature of this metastable phase. The thermal data (low ΔH and no significant hysteresis) merely suggest that this phase retains a high degree of plasticity.

In light of our findings, we believe that the complications observed with enantiomer mixtures on the first heating result from some non-homogeneity of the solid samples, and not from the existence of a solid solution as previously assumed. A possible explanation for this non-homogeneity is that a crystalline transformation occurs when the samples are heated. However, efforts to find evidence (by IR or X-ray analysis) of the existence of another crystalline phase were unsuccessful. We therefore conclude that racemic cis-π-camphanic acid simply undergoes a conglomerate-plastic crystal transformation. This transition corresponds both to an orientational disordering of the molecules on their sites and to a molecular diffusion phenomenon in the crystal. In such a situation, attainment of thermodynamic equilibrium may be delayed. Crystallization from the plastic phase, as crystallization from melt, is likely to give very small crystals, intimately mixed, which certainly facilitate the equilibrium.

III. CRYSTALLOGRAPHIC STRUCTURE

Structure of the enantiomer at low temperature

Intensities were registered with a Nicolet diffractometer (λ Mo) at room temperature.

The crystal is hexagonal; cell parameters $a = b = 6.862(2)$ Å, $c = 36.30(1)$ Å, space group $P6_1$ (6 molecules per unit cell). The structure was solved by direct methods using MULTAN program.[4] The final agreement factors are $R_w = 0.037$, $R = 0.035$ (645 intensities—hydrogen atoms positioned but not refined).

Figure 3 shows the conformation of the molecule (projection on the plane C7 O1 C5) and confirms the *cis* structure of **2**. Distances, angles and dihedral angles are given in Table I (coordinates can be sent on request).

Molecules deduced by 6_1 screw axis are linked by hydrogen bonds (O9 . . . O'13 = 2.67 Å).

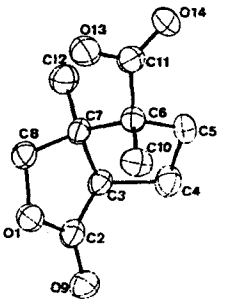

FIGURE 3 Projection of the molecule on the plane C7 O1 C5.

The stacking of molecules is very close to a compact stacking. Each molecule has twelve neighbours: six at the same z_0 level (d = 6.86 Å), three above at z_0 + 1/6 and three below at z_0 − 1/6 (d = 7.25 Å ± 0.25).

Racemic crystals are identical to enantiomer crystals: this fact confirms that the racemate is a conglomerate.

High temperature plastic form

Although the plastic phase has been observed by optical microscopy,[5] we have not been able to study its crystallographic structure. The crystals, even sealed in capillary tubes, sublimed before the transition temperature was reached.

Nevertheless, we can suggest a reasonable structure which is derived from the low-temperature structure (Figure 4). In the plastic phase, the molecules are orientationally disordered and rotate around their gravity centers (G_i:z_0 + i/6). The molecular sites at z_0, z_0 + 2/6 and z_0 + 4/6 should be equivalent and could be deduced by a translation $c' = a/3$. This leads to an hexagonal compact plastic structure with $a' = b' \# a$ and $c' \# c/3$; c'/a' should be very close to 1.73, the characteristic value of an hexagonal compact structure.

IV. CONCLUSION

The phase diagram between enantiomers of cis-π-camphanic acid has been revised. Although certain aspects previously published are confirmed—a conglomerate as the crystalline phase at low temperature and a plastic phase at high temperature—there is no evidence of a solid solution domain between these two phases. The crystal structure

TABLE I

Distances in Å (e.s.d 0.08 Å), angles and torsion angles in degrees (e.s.d 0.7°)

O1	C2	1.31	C2	O1	C8	110.6
C2	C3	1.49	O9	C2	O1	120.1
			O9	C2	C3	127.4
			O1	C2	C3	112.5
C3	C4	1.54	C2	C3	C7	103.2
			C2	C3	C4	116.4
			C7	C3	C4	108.1
C4	C5	1.54	C5	C4	C3	105.0
C5	C6	1.54	C4	C5	C6	104.9
C6	C7	1.57	C11	C6	C5	112.6
			C11	C6	C10	108.6
			C11	C6	C7	110.7
			C5	C6	C10	109.6
			C5	C6	C7	101.7
			C10	C6	C7	113.5
C7	C8	1.54	C3	C7	C12	114.0
			C3	C7	C8	102.7
			C3	C7	C6	102.5
			C12	C7	C8	111.0
			C12	C7	C6	111.3
			C8	C7	C6	114.8
C8	O1	1.45	O1	C8	C7	105.7
O9	C2	1.23				
C10	C6	1.56				
C11	C6	1.50	O14	C11	O13	122.9
			O14	C11	C6	124.5
			O13	C11	C6	112.5
C12	C7	1.54				
O13	C11	1.33				
O14	C11	1.20				

O1	C2	C3	C7	15.1
C2	C3	C7	C8	−21.7
C3	C7	C8	O1	21.8
C7	C8	O1	C2	−13.6
C8	O1	C2	C3	−1.1
C3	C4	C5	C6	24.3
C4	C5	C6	C7	−40.1
C5	C6	C7	C3	39.7
C6	C7	C3	C4	−25.6
C7	C3	C4	C5	1.4

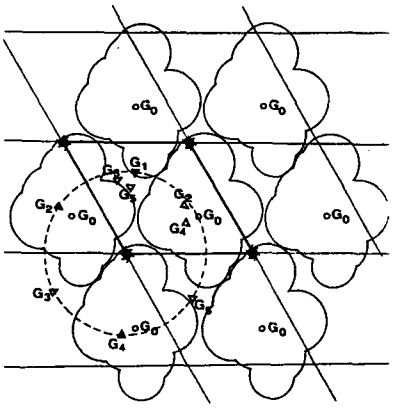

FIGURE 4 Section of the Van der Waals volume of molecules in the plane of the gravity center G_0 (z_0) (○). On the one hand we represent the gravity centers of the molecules, deduced from G_0 by 6_1 screw axis (G_i:z_0 + i/6) (△), and on the other hand the gravity centers of the six molecules inside the bold line cell.

of the enantiomer (space group $P6_1$) supports this result: it does not seem possible with such a structure to go from D crystals to L crystals by a continuous substitution process as it happens when there is a continuous miscibility in the solid state.[6,7]

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References

1. J. Lajzerowicz-Bonneteau, J. Lajzerowicz and D. Bordeaux, *Phys. Rev. B*, **34**, 6453 (1986).
2. J. Jacques, A. Collet and S. H. Wilen, *Enantiomers, Racemates, and Resolutions* (J. Wiley & Sons, New York, 1981).
3. A. Collet, M.-J. Brienne and J. Jacques, *Bull. Soc. Chim. Fr.*, 127 (1972).
4. G. Germain, P. Main and M. M. Wollfson, *Acta Cryst. A*, **27**, 368 (1971).
5. P. Cuvelier, *Thesis*, University of Lille (1986).
6. B. Chion, J. Lajzerowicz-Bonneteau, D. Bordeaux, A. Collet and J. Jacques, *J. Phys. Chem.*, **82**, 2682 (1978).
7. J. Lajzerowicz-Bonneteau, B. Chion and J. Lajzerowicz, *J. Chem. Phys.*, **74**, 3500 (1981).