Articles

Temperatures and Enthalpies of Solid−Solid and Melting Transitions of the Odd-Numbered *n*-Alkanes C_{21}, C_{23}, C_{25}, C_{27}, and C_{29}

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Very high purity samples of normal pentacosane and heptacosane are made by synthesis: the procedures for the C_{25} and C_{27} synthesis and the original conditions of their purification, particularly using the extraction by supercritical carbon dioxide, are described. Measurements of temperatures and enthalpies of the solid−solid transitions and of the melting transition were carried out by differential scanning calorimetry on the C_{25} and C_{27} synthetic samples and the odd-numbered homologous *n*-alkanes (from C_{21} to C_{29}). The results show the importance of the effect of the impurities, particularly for the δ and γ crystal−crystal transition temperatures of C_{25} and C_{27}. Several current data of the literature are also shown concerning the temperatures and the enthalpies of solid−solid and melting transitions of these five *n*-alkanes.

Introduction

Because of the importance of the *n*-paraffins in petroleum technology, numerous studies have been carried out to determine the thermodynamic data of pure *n*-alkanes (hereafter denoted by C_n) (Achour et al., 1981; Andon et al., 1976; Atkinson et al., 1969; Barbillon et al., 1991; Bonsor et al., 1997; Bosselet et al., 1983; Broadhurst, 1962; Domalski et al., 1990; Domanska et al., 1999; Doucet et al., 1981; Doucet et al., 1984; Dreisbach, 1959; Fredricks, 1986; Hasnoui et al., 1998; Heyding et al., 1990; Hoffman et al., 1953; Jin et al., 1991; Josefiak et al., 1977; Lourdin, 1991; Maroncelli et al., 1982; Mazee, 1948; Mazee, 1949; Messerly et al., 1967; Parks et al., 1929; Parks et al., 1930; Robles et al., 1998; Schaerer et al., 1955; Schmidt et al., 1941; Seyer et al., 1944; Sirota et al., 1993; Snyder et al., 1981; Ungar, 1983) and their binary mixtures (Achour et al., 1981; Achour et al., 1992; Achour-Boudjema et al., 1996; Bosselet et al., 1983; Doucet et al., 1984; Ghogomu et al., 1997; Jouti et al., 1996; Nouar et al., 1997; Oonk et al., 1998; Robles et al., 1996; Sabour et al., 1995; Srivastava, 2000). The odd-numbered homologues C_{2p+1}, which display increasing polymorphism as the temperature increases, occupy a large place in the literature (Achour et al., 1981; Barbillon et al., 1991; Bonsor et al., 1997; Bosselet et al., 1983; Broadhurst, 1962; Domalski et al., 1990; Domanska et al., 1994; Doucet et al., 1981; Doucet et al., 1984; Dreisbach, 1959; Ewen et al., 1974; Fredricks, 1986; Hasnoui et al., 1998; Heyding et al., 1990; Hoffman et al., 1953; Josefiak et al., 1977; Maroncelli et al., 1985; Mazee, 1948; Mazee, 1949; Müller, 1932; Nozaki et al., 1995; Parks et al., 1929; Piesczek et al., 1974; Robles et al., 1998;

Schaerer et al., 1955; Schmidt et al., 1941; Seyer et al., 1944; Sirota et al., 1993; Snyder et al., 1981; Srivastava et al., 1993; Strobl et al., 1974; Ungar, 1983; Verdonk, 1938). The aim of this article is to determine the impurity effects (Ghogomu et al., 1990) on the temperatures and the enthalpies of solid−solid and solid−liquid transitions, using commercial and synthetic pure C_n, and to point to several thermodynamic literature data for the odd-numbered homologous series C_{21} to C_{29}.

Experimental Section

Commercial C_{21}, C_{23}, C_{25}, C_{27}, and C_{29} were purchased from Fluka (purity $\geq$ 98% (GC)).

General Description of the Sample Synthesis (C_{25} and C_{27}). Azelaic acid, thionyl chloride, 1-bromooctane, and 1-bromononane, with a purity $\geq$ 99%, were purchased from Aldrich and used without purification. Zinc chloride was obtained from Fluka (purity $\geq$ 98%).

First Step of the Chemical Synthesis: Azelaoyl Chloride. A mixture of 49.5 g of the diacid and 78 mL of thionyl chloride was refluxed for 24 h at 80 °C. The excess of thionyl chloride was removed by distillation under atmospheric pressure. Distillation under reduced pressure (98 °C, 53.3 Pa) provides 57 g (molar yield: 96%) of pure azelaoyl chloride.

The infrared spectrum exhibited a strong peak in the carbonyl region, at 1799 cm^{-1}, assigned to acid chloride.

Second Step of the Chemical Synthesis: 9,17-Pentacosanedione and 10,18-Heptacosanedione. The chemical synthesis of the two alkanes was carried out simultaneously.

(i) Grignard Reagents. 1-Bromooctane (35 mL) (or 1-bromononane (41 mL)) and an excess of magnesium turnings

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(5 g) were allowed to react in 130 mL of anhydrous ether to give the Grignard reagents.

(ii) Diketones. Zinc chloride (21.6 g, 0.158 mol) was weighed into a 250 mL three-necked round-bottomed flask. The mouth of the flask was connected to a vacuum pump. The system was evacuated and dried. The zinc chloride was slowly fused to a clear melt. After the flask was cooled to room temperature in a vacuum, the vacuum pump line was removed and 70 mL of anhydrous ether was added. The mixture in the closed system was stirred magnetically until the fused zinc chloride had dissolved and the solution became colorless. To this solution, the Grignard reagent was added rapidly. A thick, gray paste was obtained with strong refluxing. After 20 min of stirring, ether was removed and 33 mL of anhydrous benzene was added to the pasty mixture. Azelaoyl chloride (11 mL) in anhydrous benzene (140 mL) was added to the organozinc reagent over a period of 15 min. The solution was stirred and refluxed for 3 h under nitrogen. The mixture (gray paste) was then hydrolyzed with 2 M hydrochloric acid. The organic layer was separated, a solid was recovered, and benzene was removed on a rotary evaporator. The crude products were washed with water, dried, and purified by recrystallization from benzene. 9,17-Pentacosanedione was obtained in 60 mass % yield (mp 96 °C), and 10,18-heptacosanedione, in 56 mass % yield (mp 99 °C).

The diketones were characterized by infrared spectroscopy (wave number corresponding with C=O linked to CH$_2$), thin-layer chromatography (one spot for each product), and ^{13}C NMR.

Third Step of the Chemical Synthesis: C$_{25}$ and C$_{27}$. 9,-17-Pentacosane dione (10.6 g) (or 11.4 g of 10,18-heptacosanedione), 25 mL of hydrazine monohydrate, 25 mL of glacial acetic acid, and 305 mL of 1-octanol were refluxed under stirring at 140−150 °C for 9 h. The water formed and the excess of hydrazine were removed with a Dean−Stark apparatus. A solution of sodium octanolate (11 g of sodium in 120 mL of 1-octanol) was added to the hydrazone.

The mixture was then refluxed for 24 h. The oil bath temperature was increased until 180 °C. The cold mixture was neutralized with 4 M HCl. The organic phase was evaporated to dryness in a vacuum (∼133 Pa). The residual semisolid was crystallized from ethanol to give a white solid which was not pure: the main impurities were unreduced ketones and alcohols formed by reduction of carbonyl groups. The purification was monitored by infrared spectroscopy: after several recrystallizations in dichloro-1,2-ethane, the C=O band disappeared but weak OH bands remained; TLC showed two weak impurity spots.

Final purification was achieved by column chromatography on silica gel (eluent toluene): fractions with one spot were collected together and vacuum-dried to eliminate the solvent. Synthetic C$_{25}$ and C$_{27}$ were obtained: C$_{25}$ yield 32 mass %, mp 53 °C; C$_{27}$ yield 29 mass %, mp 59 °C.

Purification by Supercritical Carbon Dioxide Extraction. The solid feed was introduced in the autoclave, with a stainless steel frit at the outlet column (height, 30 cm; internal diameter, 23 mm); then the autoclave was closed. Carbon dioxide ($P = 5$ MPa, $T = 20$ °C) was cooled ($T = 5$ °C), pumped ($P_{max} = 25$ MPa, CO$_2$ flow rate(max) = 3.5 kg·h^{-1}), and then heated to be a supercritical fluid or a liquid. It flows through the thermostated extraction column. At the outlet column, the mixture CO$_2$−solutes was expanded through three valves and the components were separated in cyclonic separators. Finally CO$_2$ was vented through a rotameter and a gasmeter. A characteristic of the process is to withdraw the solutes in atmospheric

Table 1. Temperatures and Enthalpies of Solid−Solid Transitions and the Melting of C$_{21}$: Comparison between the Literature Data (Transition Temperatures and Enthalpies) of C$_{21}$ and the Experimental Values ($\Delta T = \pm 0.1$ K, $\Delta(\Delta H_{o-d}) = \pm 140$ J·mol^{-1}, $\Delta(\Delta_{fus}H) = \pm 450$ J·mol^{-1}) of This Work for C$_{21}$

ref	% purity	T_{o-d} K	fusion T_{fus} K
Barbillon et al., 1991	99	305.1	313.4
Broadhurst et al., 1962		306.15	313.15
Doucet et al., 1981	97	305.7	313.7
Dreisbach, 1959			313.65
Heyding et al., 1990	99	305.15	312.15
Maroncelli et al., 1985[a]	99.6	305.75	
Mazee, 1948/1949[a]		305.95	313.5
Schaerer et al., 1955[a]	99.9	305.65	313.35
Schmidt et al., 1941			312.6
Seyer et al., 1944			313.6
Sirota et al., 1993	99	303.95	313.25
this work	≥98	303.99	313.16

ref		ΔH_{o-d} J·mol^{-1}	$\Delta_{fus}H$ J·mol^{-1}	$\Delta H_{T_{o-d}}^{T_F}$ J·mol^{-1}
Barbillon et al., 1991	99	16 500	46 000	75 500
Bonsor et al., 1997		15 600		
Broadhurst et al., 1962		15 481	47 698	
Dreisbach et al., 1959			47 697	
Maroncelli et al., 1985[a]	99.6	17 154	47 698	
Mazee et al., 1948/1949[a]		15 070		70 710
Schaerer et al., 1955[a]	99.9	15 481	47 698	70 425
this work	≥98	13 356	45 208	

[a] Quoted in *TRC Databases*, 1998.

conditions whenever necessary. The results of the purification by this method have already been described in the literature (Gandolfo et al., 1999).

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 P spectrometer in deuteriochloroform solution. Chemical shifts were given in δ downfield from TMS. The FTIR spectra were measured with a Nicolet 210 spectrometer.

Products were analyzed by gas chromatography on a Carlo Erba GC 6000 equipped with a capillary column (WCOT ULTI-METAL, 10 m, 0.53 mm). The FID temperature was 330 °C, with on-column injection. The oven temperature was held at 50 °C for 3 min; then a temperature gradient was operated (10 K·min^{-1}), and finally an isotherm was maintained at 300 °C. The samples were diluted in 0.5 mL of n-C$_7$, and 0.5 μL of solution was injected.

The calorimetric measurements were performed using a differential scanning calorimeter SETARAM DSC III of the Tian Calvet type. The samples were initially melted and cooled in the measuring crucible. The DSC analyses were carried out with a heating rate of 0.5 K·min^{-1} from 293.15 K to 338.15 K. These experimental conditions allowed the measurements of the onset and final temperatures of a transformation: the temperatures were determined with an accuracy of ±0.1 K, according to the method of measurements established by Courchinoux et al. (1988). The enthalpies were obtained from the surface area defined by the peaks and using a linear baseline between the onset and the end of the transformations with a relative accuracy of 1%. The apparatus was calibrated with the help of the thermodynamic data of alumina (Ditmars et al., 1982), of pure water, and of pure toluene. Experimental data of the commercial samples are in good agreement with the literature data (Tables 1−5), and this agreement justifies the experimental method used.

Table 2. Temperatures and Enthalpies of Solid−Solid Transitions and the Melting of C_{23}: Comparison between the Literature Data and the Experimental Values of This Work ($\Delta T = \pm 0.1$ K, $\Delta(\Delta H_{o-d}) = \pm 200$ J·mol^{-1}, $\Delta(\Delta_{fus}H) = \pm 500$ J·mol^{-1})

ref	% purity	T_δ (K)	T_{o-d} (K)	T_{RI} (K)	T_{RII} (K)	T_{fus} (K)
Barbillon et al., 1991	99		313.5			320.8
Broadhurst et al., 1962			313.15			321.15
Domalski et al., 1990						319.5
Dreisbach, 1959						320.75
Fredricks, 1986	99		313.15			319.95
Heyding et al., 1990	99		311.15			320.15
Maroncelli et al., 1985[a]	99.6		313.6			
Mazee, 1948/1949[a]			313.75			320.5
Schaerer et al., 1955[a]	99.6		313.65			320.65
Seyer et al., 1944						320.6
Sirota et al., 1993	99		314.45			
Hasnaoui et al., 1988	99				318	
Ungar, 1983	99	307.7	312.7	314	317.7	
Robles et al., 1998	99.3	310.5	312.4	314.8	317.9	320.3
this work	≥98	311.15	313.85		318.65	320.91

ref	% purity	ΔH_δ (J·mol^{-1})	ΔH_{o-d} (J·mol^{-1})	ΔH_{RII} (J·mol^{-1})	$\Delta_{fus}H$ (J·mol^{-1})	$\Delta H_{T_{o-d}}^{T_F}$ (J·mol^{-1})
Barbillon et al., 1991	99		21 500		52 250	84 000
Bonsor et al., 1997			21 927			
Bosselet et al., 1983[a]	99					76 061
Broadhurst et al., 1962			21 757		53 974	
Domalski et al., 1990						
Fredricks, 1986	99		25 808		52 839	
Maroncelli et al., 1985[a]	99.6		23 430			
Mazee, 1948/1949[a]			22 604			81 170
Schaerer et al., 1955[a]	99.6		21 757			
Ungar, 1983		320		320	53 974	
Robles et al., 1998	99.3	320<	19 600	320<	52 600	
this work	≥98	in the o−d peak	23 063		50 863	

[a] Quoted in *TRC Databases*, 1998.

C_n Structural Behavior versus Temperature: Literature Results

The crystalline structure of pure C_n was described by Müller and Saville (1925), and Müller (1932) observed the existence of a solid−solid transition by X-ray diffraction, when the temperature increases, with the appearance of disordered phases that present molecular movements of the "Rotator" type. The crystallographic structures of "low temperature" phases have been recently specified by Craig et al. (1994) and Chevallier et al. (1999), who have respectively clarified the space groups and the correlations between the crystalline long c-parameter and the number of carbon atoms of pure C_n, particularly concerning the odd-numbered C_{2p+1} and their phase, denoted $\beta_0(Pbcm)$, whose space group was determined by Smith (1953).

The structural behavior of pure odd-numbered C_{2p+1} ($21 \leq 2p + 1 \leq 29$), as a function of the temperature, has been the subject of numerous publications in the literature, leading to the following results (Doucet et al., 1984; Ewen et al., 1974; Hasnoui et al., 1988; Maroncelli et al., 1982; Maroncelli et al., 1985; Nozaki et al., 1995; Piesczek et al., 1974; Robles et al., 1998; Sirota et al., 1993; Snyder et al., 1981; Sirota et al., 1995; Srivastava et al., 1993; Strobl et al., 1974; Ungar, 1983; Ungar et al., 1985):

(i) δ-Transition. C_{23}, C_{25}, C_{27}, and C_{29} undergo the transition highlighted and called the δ-transition by Snyder et al. (1981). According to Nozaki et al. (1995), this crystal ↔ crystal transition leads to the phase denoted $\beta_0'(Pbnm)$.

(ii) γ-Transition. A second crystal ↔ crystal transition has been observed in C_{25}, C_{27}, and C_{29} by Piesczek et al. (1974) and by Maroncelli et al. (1982), who denoted it transition as γ. It corresponds to the appearance of a monoclinic phase, called B by Piesczek et al. (1974), IV by Maroncelli et al. (1982), and M* by Robles et al. (1998).

The monoclinic space group, Aa, of this third ordered phase of "low temperatures" has been determined by Ewen et al. (1974), Piesczek et al. (1974), and Strobl et al. (1974) and called B(Aa).

(iii) Order ↔ Disorder Transition. This transition, which gives a major thermal effect (Figures 1 and 2), corresponds to the appearance of the following disordered phases:

(a) orthorhombic $\beta(Fmmm)$ (Ungar, 1983; Ungar et Masic, 1985) for C_{21}, C_{23}, and C_{25}. When the temperature increases, the molecules of this $\beta(Fmmm)$ phase are driven by a movement of the "Rotator" type, denoted RI. Hereafter, this order−disorder transition is denoted the o−d transition.

(b) triclinic RIII (Doucet et al., 1984; Robles et al., 1998; Sirota et al., 1993; Sirota et al., 1995; Srivastava et al. 1993) for C_{27} and C_{29}.

(iv) Last Solid−Solid Transition. Just below the melting point, the following phases appear:

(a) rhombohedral α-RII ($R\bar{3}m$) (Ungar, 1983; Ungar and Masic, 1985) for C_{23} and C_{25}.

(b) monoclinic RIV (Doucet et al., 1984; Robles et al., 1998; Sirota et al., 1993; Sirota et al., 1995; Srivastava et al., 1993) for C_{27} and C_{29}.

In summary, the phase succession, when the temperature increases, is as shown in Scheme 1.

Results

Figures 1−4 show the DSC curves obtained for C_{21}, C_{23}, C_{25}, C_{27}, and C_{29}. The two higher thermal peaks correspond respectively to the order−disorder transition, denoted o−d transition, and to the fusion:

(a) The δ-transition is not observed for C_{21} (Figure 1). It appears for C_{23} just below the order−disorder transition

Figure 1. DSC curve of C_{21} with increasing temperature: observation of the o−d transition $\beta(Pbcm) \rightarrow \beta(Fmmm)$ (first peak) and of the melting (second peak).

Scheme 1

$$C_{21}\beta_O \text{ (Pbcm)} \qquad \xrightarrow{\text{o-d}} \beta(Fmmm) \Rightarrow \beta\text{-RI(Fmmm)} \qquad \rightarrow \text{liquid}$$

$$C_{23}\beta_O \text{ (Pbcm)} \xrightarrow{\delta} \beta'_O \text{ (Pbnm)} \qquad \xrightarrow{\text{o-d}} \beta(Fmmm) \Rightarrow \beta\text{-RI(Fmmm)} \rightarrow \alpha RII \text{ } (R\bar{3}m) \rightarrow \text{liquid}$$

$$C_{25}\beta_O(\text{Pbcm}) \xrightarrow{\delta} \beta'_O \text{ (Pbnm)} \xrightarrow{\gamma} B(Aa) \xrightarrow{\text{o-d}} \beta(Fmmm) \Rightarrow \beta\text{-RI(Fmmm)} \rightarrow \alpha RII \text{ } (R\bar{3}m) \rightarrow \text{liquid}$$

$$C_{27}\beta_O(\text{Pbcm}) \xrightarrow{\delta} \beta'_O \text{ (Pbnm)} \xrightarrow{\gamma} B(Aa) \xrightarrow{\text{o-d}} \qquad RIII \quad \rightarrow \quad RIV \qquad \rightarrow \text{liquid}$$

$$C_{29}\beta_O(\text{Pbcm}) \xrightarrow{\delta} \beta'_O \text{ (Pbnm)} \xrightarrow{\gamma} B(Aa) \xrightarrow{\text{o-d}} \qquad RIII \quad \rightarrow \quad RIV \qquad \rightarrow \text{liquid}$$

ordered phases   disordered

"CRYSTAL"   PHASES

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where → denotes first-order transitions and ⇒ denotes higher-order transitions.

peak (Figure 2a); for C_{25}, C_{27}, and C_{29}, the thermal effect of the δ-transition is clearly separated from the o−d transition thermal accident (Figure 2b−d).

(b) The γ-transition is highlighted in C_{27} and C_{29} (Figure 2c and d)

(c) The last solid−solid transition, whose enthalpy is very low, is observed only in C_{23} (Figure 2a).

The experimental data of temperatures and enthalpies of solid−solid and solid−liquid transitions are reported in Tables 1−5, in which they are compared with the literature data.

Taking account of the purity problems, the thermodynamic values of commercial samples are comparable with those of the literature. Nevertheless, concerning the solid−solid transition and melting temperatures of C_{25} and C_{27}, differences appear between the literature values or our own experimental results, determined from the commercial samples, and those measured on the synthetic samples

(Tables 3 and 4, Figures 3 and 4): in general the latter are higher. More particularly, a significant variation is observed for the δ-transition temperature, which is very sensitive to the presence of impurities. The phenomenon has already been highlighted by Sabour et al. (1995) and by Jouti et al. (1996), respectively, in the binary $C_{23}-C_{24}$ and $C_{21}-C_{23}$ diagrams. These authors note a very strong decrease of the δ-transition temperature when the C_{24} or C_{21} molar concentration increases from that of pure commercial C_{23} (about 7 K/1% molar increase of C_{24} or C_{21}), and they attribute it to an increase in the disorder of the crystallographic structure of C_{23}, produced by the presence of a small amount of another C_n ($n < 23$ or $n > 23$).

For the synthetic C_{25} and C_{27}, the δ-transition temperatures are higher than the values of the literature and our own measurements on the commercial samples (Tables 3 and 4, Figures 3 and 4). Moreover, the addition of 0.3% molar of C_{23} into the synthetic C_{25} sample provokes a

Figure 2. DSC curves of C_{23} (2a), C_{25} (2b), C_{27} (2c), and C_{29} (2d).

Figure 3. Influence of the impurities in the pure C_{25} on the δ-transition (first peak) and o–d transition (second peak) temperatures: the sample obtained by synthesis presents the higher solid–solid transition temperatures; when 0.3 molar % of C_{23} is added to the C_{25} synthetic sample, these transition temperatures decrease, but they are higher than those of the commercial C_{25}. The γ-transition is not detected in the samples of high purity.

decrease in the δ-transition temperature of 0.6 K (Table 3, Figure 3).

The effect of impurities is also observed for the γ-transition temperatures. Concerning C_{25}, Ungar (1983), Snyder et al. (1981), and Robles et al. (1998) observed this transition at a few tenths of Kelvin below the o–d transition (Table 3). Like other authors (Achour et al., 1981; Barbillon et al., 1991; Bosselet et al., 1983; Broadhurst, 1962; Dreisbach, 1959; Fredricks, 1986; Heyding et al., 1990; Maroncelli, 1985; Parks et al., 1929, 1930; Seyer, 1944; Sirota et al., 1993), we do not detect the γ-transition for the three C_{25} samples studied here (commercial No. 1, synthetic No. 2, and synthetic with 0.3% molar of C_{23} No.

3) (Table 3, Figures 2b and 3): either it is mixed with the o–d transition peak or the monoclinic B(*Aa*) phase appears in the C_{25} because of the impurities, and so it is not present in the very pure C_{25}. For the two C_{27} samples, the thermal effect of the γ-transition is clearly separated from the o–d transition peak (Figures 2c and 4); the γ-transition temperature of the synthetic sample is higher by 0.8 Kelvin in regard to that of the commercial C_{27} (Table 4, Figure 4).

According to these observations, it appears that

(a) the synthetic C_{25} and C_{27} present a higher purity than the commercial products, currently used to determine thermodynamic data, and
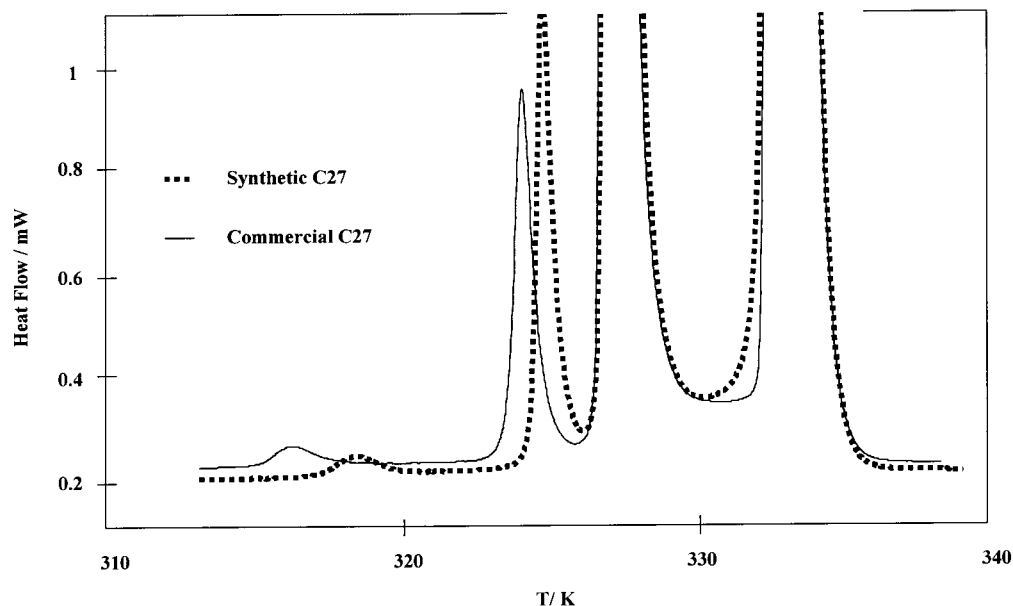
Figure 4. Influence of the impurities in C_{27}. As in C_{25}, the solid−solid transition temperatures (δ-transition, first peak; γ-transition, second peak) increase as the purity increases.

Table 3. Temperatures and Enthalpies of Solid−Solid Transitions and the Melting of C_{25}: Comparison between the Literature Data and the Experimental Values of This Work ($\Delta T = \pm 0.1$ K, $\Delta(\Delta H_{o-d}) = \pm 280$ J·mol^{-1}, $\Delta(\Delta_{fus}H) = \pm 500$ J·mol^{-1})[a]

ref	% purity	T_δ K	T_γ K	T_{o-d} K	T_{RI} K	T_{RII} K	T_{fus} K
Barbillon et al., 1991	99			320			326.7
Bosselet et al., 1983[b]	99			319.85			326.25
Broadhurst et al., 1962				320.15			326.7
Domanska et al., 1999	98			319.45			327.20
Dreisbach, 19665/1969							326.85
Fredricks, 1986	99			319.25			325.85
Heyding et al., 1990	99			318.15			325.15
Maroncelli et al., 1985[b]	99.6			319.9			
Parks et al., 1929[b]				319.41			326.45
Achour et al., 1998				320.15			326.05
Schaerer et al.,1955[b]	99.8						326.65
Seyer et al., 1944							326.5
Sirota et al., 1981	99			320.15		322.05	326.5
Ungar, 1983	99	311.7	319.4	321		321.3	
Snyder et al., 1981		310.3	319.9				
Robles et al., 1998	99.1	310.5	319.4	320	321.2	322.6	326.4
no. 1 this work[a]	≥98	311.9		320.66			327.03
no. 2 this work[a]		314.9		320.80			327.13
no. 3 this work[a]		314.3		320.70			327.08

ref		ΔH_δ J·mol^{-1}	ΔH_γ J·mol^{-1}	ΔH_{o-d} J·mol^{-1}	ΔH_{RII} J·mol^{-1}	$\Delta_{fus}H$ J·mol^{-1}
Barbillon et al., 1991	99			26 500		56 750
Bonsor et al., 1997				26 352		
Bosselet et al., 1983[b]	99			25 235		56 605
Broadhurst et al., 1962				25 941		57 739
Dreisbach, 1959						57 738
Fredricks, 1986	99			28 186		56 519
Maroncelli et al., 1985[b]	99.6			28 451		
Achour et al., 1998				27 343		56 702
Schaerer et al., 1955[b]	99.8			26 066		57 739
Snyder et al., 1981				28 400		
Ungar, 1983	99	350			350	
Sirota et al., 1993	99				250	57 170
Robles et al., 1998	99.1	350≤	350	23 600	350≤	57 180
no. 1 this work[a]	≥98	281		27 445		56 663
no. 2 this work[a]		289		27 630		57 122
no. 3 this work[a]		277		27 502		56 915

[a] No. 1, commercial sample; no. 2, synthetic sample; no. 3, synthetic sample with 0.3% of C_{23}. [b] Quoted in *TRC Databases*, 1998.

Table 4. Temperatures and Enthalpies of Solid−Solid Transitions and the Melting of C_{27}: Comparison between the Literature Data and the Experimental Values of This Work ($\Delta T = \pm 0.1$ K, $\Delta(\Delta H_{o-d}) = \pm 280$ J·mol^{-1}, $\Delta(\Delta_{fus}H) = \pm 620$ J·mol^{-1})[a]

ref	% purity	T_δ K	T_γ K	T_{o-d} K	T_{RIV} K	T_{fus} K
Broadhurst et al., 1962				325.75		331.55
Doucet et al., 1981				324.75		330.95
Domanska et al., 1999	98			327.40		331.85
Dreisbach, 1959						332.15
Fredricks, 1986	99			326.85		331.15
Heyding et al., 1990	99		320.15	325.15		331.15
Hoffman et al., 1953	96			325.85		331.83
Josfiak et al., 1977	99		319.5	326.7		332.7
Lourdin, 1991	99		318.5	325.6		331.6
Maroncelli et al., 1985[b]	99.6	309.8	320.8	326.5		
Schaerer et al., 1955[b]	99		300.25	326.15		331.15
Seyer et al., 1944					328.55	332.3
Sirota et al., 1993	99		324.95	326.95		
Snyder et al., 1981		309.8	320.8	326.5	327.9	
Robles et al., 1998	99.1	312.9	322.3	325.9		331.6
Verdonk, 1938				321.15		332.15
no. 1 this work[a]	≥98	315.24	323.64	326.75		332.37
no. 2 this work[a]		317.25	324.44	326.82		332.38

ref		ΔH_δ J·mol^{-1}	ΔH_γ J·mol^{-1}	ΔH_{o-d} J·mol^{-1}		$\Delta_{fus}H$ J·mol^{-1}
Broadhurst et al., 1962						60417
Dreisbach, 1959						60420
Fredricks, 1986	99			31384		63086
Lourdin, 1991	99		2200	26300		59000
Maroncelli et al., 1985[b]	99.6	293	2427	27196		
Schaerer et al., 1955[b]	99		2385	26568		60417
Robles et al., 1998	99.1	270	2470	27100		62800
Verdonk, 1938				19646		58102
no. 1 this work[a]	≥98	283	2523	27778		61697
no. 2 this work[a]		246	2531	27407		62024

[a] No. 1, commercial sample; no. 2, synthetic sample. [b] Quoted in *TRC Databases*, 1998.

Table 5. Temperatures and Enthalpies of Solid−Solid Transitions and the Melting of C_{29}: Comparison between the Literature Data and the Experimental Values of This Work ($\Delta T = \pm 0.1$ K, $\Delta(\Delta H_{o-d}) = \pm 300$ J·mol^{-1}, $\Delta(\Delta_{fus}H) = \pm 670$ J·mol^{-1})

ref	% purity	T_δ K	T_γ K	T_{o-d} K	T_{fus} K
Broadhurst et al., 1962	99			330.95	336.15
Doucet et al., 1981	99.6			329.05	333.65
Dreisbach, 1959	99.5				336.85
Heyding et al., 1990				330.15	335.15
Maroncelli et al., 1985[a]	99			331.1	
Schaerer et al., 1955[a]	>99.5	310.2	322.4	331.35	336.55
Seyer et al., 1944				330.25	336.5
Sirota et al., 1993				330.75	336.55
this work	≥99.5	314.17	325.41	331.77	336.8

ref		ΔH_δ J·mol^{-1}	ΔH_γ J·mol^{-1}	ΔH_{o-d} J·mol^{-1}	$\Delta_{fus}H$ J·mol^{-1}
Bonsor et al., 1997				31 766	
Broadhurst, 1962				31 547	66 107
Maroncelli et al., 1985[a]	99.6	293	2594	30 125	
Schaerer et al., 1955[a]	99.5			29 706	66 107
this work	≥99.5	248	2468	30 026	66 939

[a] Quoted in *TRC Databases*, 1998.

(b) the monoclinic B(Aa) phase stability is more sensitive to impurities in C_{25} than in C_{27}, as is the $\beta'_0(Pbnm)$ phase stability in C_{23} with regard to that of C_{25}.

Conclusion

We make use of a new procedure of C_n synthesis and purification that leads to C_{25} and C_{27} of very high purity. From these samples, the impurity effects have particularly been highlighted for the δ- and γ-transition temperatures which increase with the purity of the samples: the δ-transition, that is not present for C_{21}, tends to merge with the order−disorder o−d transition for C_{23} and disappears when its purity increases. The same behavior occurs for the γ-transition in C_{25}, which is not observed in the synthetic samples. The C_n chain length has an influence on the existence of these solid−solid transitions, as do the impuri-

ties, particularly for the δ-transition in C_{23} and the γ-transition in C_{25}. As it is very difficult to determine the amount of impurities in these C_n by chromatographic methods, the measurements of the temperatures of the δ- or γ-transitions can give a relative evaluation of their state of purity.

Nomenclature

T_δ, ΔH_δ — temperature and enthalpy of the δ-transition: $\beta_0(Pbcm) \rightarrow \beta'_0(Pbnm)$

T_γ, ΔH_γ — temperature and enthalpy of the γ-transition: $\beta'_0(Pbnm) \rightarrow B(Aa)$

T_{o-d}, ΔH_{o-d} — temperature and enthalpy of the order$-$disorder transition (o$-$d transition)

T_{RI} — onset temperature of the Rotator phenomenon, RI, observed in the $\beta(Fmmm)$ disordered phase.

T_{RII}, ΔH_{RII} — temperature and enthalpy of the last solid$-$solid transition for the C_{23} and C_{25}: $\beta(Fmmm)$ in RI $\rightarrow$ α-RII($R\bar{3}m$).

T_{fus}, $\Delta_{fus}H$ — temperature and enthalpy of the melting

$\Delta H_{T_{o-d}}^{T_F}$ — enthalpy variation from the order$-$disorder transition temperature (T_{o-d}) to the melting temperature (T_{fus})

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