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Enthalpy–Entropy Compensation Combined with Cohesive Free-Energy Densities for Tuning the Melting Temperatures of Cyanobiphenyl Derivatives

Thibault Dutronc,^[a] Emmanuel Terazzi,*^[a] Laure Guénée,^[b] Kerry-Lee Buchwalder,^[a] Aureore Spoerri,^[a] Daniel Emery,^[c] Jiri Mareda,^[c] Sébastien Floquet,^[d] and Claude Piguet*^[a]

Abstract: This work illustrates how minor structural perturbations produced by methylation of 4'-(dodecyloxy)-4-cyanobiphenyl leads to enthalpy–entropy compensation for their melting processes, a trend which can be analyzed within the frame of a simple intermolecular cohesive model. The transformation of the melting thermodynamic parameters collected at variable temperatures into cohesive free-energy densities expressed at a common reference temperature results in a novel linear correlation, from which melting temperatures can be simply predicted from molecular volumes.

Keywords: cohesive energy density • cyanobiphenyl • enthalpy–entropy compensation • intermolecular interactions • melting point

Introduction and Theoretical Background

Beyond the theoretically justified Gibbs free energy relationship $\Delta G = \Delta H - T\Delta S$, which links enthalpy (ΔH) and entropy (ΔS) with free energy (ΔG) changes,^[1] the extra-thermodynamic linear enthalpy–entropy correlation [Eq. (1)] may appear almost as familiar, because of its observation in an extremely wide range of areas covering chemical, physical, and biological processes.^[2,3]

$$\Delta H_i = \alpha \Delta S_i + \gamma \quad (1)$$

The slope α has units of Kelvin and is often referred to as the compensation temperature, because all chemical proc-

esses i in a homogeneous series obeying Equation (1) display the same free-energy change γ (i.e. the compensation free energy) when conducted at this temperature.^[4] Theoretical approaches of enthalpy–entropy correlation based on statistical thermodynamics include both attempts to refute its relevance,^[5] as well as to establish its signature as the result of 1) minor perturbations of equilibrium constants,^[3] 2) partition functions governed by a Gaussian density of states^[6] or 3) underlying hidden thermodynamic processes.^[7] Recent considerations further propose some physical rationale for the operation of alternative nonlinear (rectangular hyperbolic) enthalpy–entropy compensation effects.^[8] For broad scope (bio)chemists interested in controlling and tuning intermolecular interactions and phase-transition processes, but with no intention to specialize in statistical thermodynamics, Equation (1) is particularly attractive because of its intuitive interpretation, which suggests that an increasing enthalpic benefit of bonding is logically offset by an increasing adverse entropy of restricted motion.^[9] Focusing on this idea, Williams^[10] set a general parabolic form for H/S correlations, for which the entropic cost of any association between two molecular partners is some fraction of 50–60 kJ mol⁻¹,^[9] and is a sensitive function of the exothermicity of the interaction. In most cases, the experimentally accessible range of enthalpic contributions induced by molecular perturbations is too limited for detecting significant curvature, and linear H/S compensations are acceptable approximations.^[11] Building on this concept, Ford derived with the help of Bjerrum's formalism, the two non-quantum Equations (2) and (3), which model the association between two molecular partner A and B bound by a single non-directional interaction obeying a simple harmonic potential ($u_{\min}^{A,B}$ is the well depth, $\kappa^{A,B}$ is the force constant, k_b is Boltzmann constant and $\beta = (k_b T)^{-1}$).^[12]

[a] T. Dutronc, Dr. E. Terazzi, K.-L. Buchwalder, A. Spoerri, Prof. C. Piguet
Department of Inorganic and Analytical Chemistry
University of Geneva
30 quai E. Ansermet, 1211 Geneva 4 (Switzerland)
E-mail: Emmanuel.Terazzi@unige.ch
Claude.Piguet@unige.ch

[b] Dr. L. Guénée
Laboratory of X-ray Crystallography
University of Geneva
24 quai E. Ansermet, 1211 Geneva 4 (Switzerland)

[c] Dr. D. Emery, Dr. J. Mareda
Department of Organic Chemistry
University of Geneva
30 quai E. Ansermet, 1211 Geneva 4 (Switzerland)

[d] Dr. S. Floquet
Institut Lavoisier de Versailles, UMR 8180
University of Versailles Saint-Quentin
45 av. des Etats-Unis, 78035 Versailles (France)

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$$\Delta H_{\text{asso}}^{\text{A,B}} = u_{\text{min}}^{\text{A,B}} + \frac{3}{2} k_{\text{b}} T \quad (2)$$

$$\Delta S_{\text{asso}}^{\text{A,B}} = k_{\text{b}} \ln \left[c^{\theta} \left(\frac{2\pi e}{\beta \kappa^{\text{A,B}}} \right)^{3/2} \right] \quad (3)$$

The development of Ford's harmonic potential at the minimum of a standard Lennard–Jones (12,6) attractive well satisfyingly catches the two parameters used for characterizing the intermolecular interaction operating between the two molecular partners: 1) the absolute minimum of the attractive well depth $\varepsilon = -u_{\text{min}}^{\text{A,B}}$ and 2) the critical intermolecular A...B distance r_0 at which the potential of interaction is zero (Figure 1).^[13] The consideration of the total energy of the

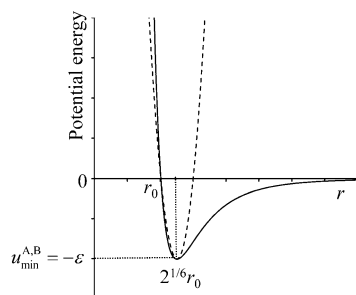


Figure 1. Representation of a Lennard–Jones (12,6) potential (full trace) with the interpretation of ε and r_0 parameters, and its harmonic approximation modelling the intermolecular interactions responsible for the formation of a AB complex. Adapted from reference [13].

harmonic oscillator for the special motion amplitude $r_0(2^{1/6} - 1)$ eventually gives Equation (4) for the force constant $\kappa^{\text{A,B}}$, estimating the capacity of the bound system to gain residual degrees of freedom.

$$\frac{\kappa^{\text{A,B}} [r_0(1 - 2^{1/6})]^2}{2} = \varepsilon \Rightarrow \quad (4)$$

$$\kappa^{\text{A,B}} = \frac{2}{(1 - 2^{1/6})^2} \frac{\varepsilon}{(r_0)^2} = - \frac{2}{(1 - 2^{1/6})^2} \frac{u_{\text{min}}^{\text{A,B}}}{(r_0)^2}$$

According to this simple model, the structural parameter r_0 represents the required hidden physicochemical process at the origin of H/S correlation.^[7,14] When r_0 is constant along a perturbation applied to the molecular AB pair (i.e. the minimum contact distance at which the interaction potential is zero is retained along the perturbation), Equation (4) predicts that the force constant $\kappa^{\text{A,B}}$, controlling the association entropy, $\Delta S_{\text{asso}}^{\text{A,B}}$ [Eq. (3)] linearly depends on the well depth $u_{\text{min}}^{\text{A,B}}$, controlling the association enthalpy $\Delta H_{\text{asso}}^{\text{A,B}}$ [Eq. (2)].^[12,15] Moreover, any change of $u_{\text{min}}^{\text{A,B}}$ induces a shift of $\kappa^{\text{A,B}}$ in the opposite direction resulting in the “natural” emergence of H/S compensation [$\alpha > 0$ in Eq. (1)]; hence $\Delta H_{\text{asso}}^{\text{A,B}}$ and $\Delta S_{\text{asso}}^{\text{A,B}}$ both decrease or both increase. Exact linear compensation as shown in Equation (1) further requires the expansion of the logarithmic function in Equa-

tion (3) as a first-order Taylor series around a central $\kappa_0^{\text{A,B}}$ estimate for the force constant of the process.^[16] A plethora of H/S compensations obeying Equation (1) have been reported for the melting of solids subjected to minor structural variations (ΔG_{m} , ΔH_{m} , ΔS_{m}),^[10,17] or during reverse condensation processes, in which isotropic liquids or liquid-crystalline phases transform into organized solids (ΔG_{asso} , ΔH_{asso} , ΔS_{asso}).^[18] These processes can be idealized as reversible n th-order chemical reactions, in which n identical monomers associate into fully assembled entities with $\Delta G_{\text{m}} = -\Delta G_{\text{asso}}$, $\Delta H_{\text{m}} = -\Delta H_{\text{asso}}$ and $\Delta S_{\text{m}} = -\Delta S_{\text{asso}}$ [Eq. (5)].



A famous example concerns the melting of linear saturated hydrocarbons $\text{C}_n\text{H}_{2n+2}$ of increasing length ($n > 1$), in which two terminal methyl tripods are separated by an increasing number ($n-2$) of methylene rotors.^[19] The plot of ΔH_{m} ($\text{C}_n\text{H}_{2n+2}$) versus ΔS_{m} ($\text{C}_n\text{H}_{2n+2}$) indeed displays H/S compensation (Figure 2a). At the melting temperature T_{m} , the phase equilibrium condition requires $\Delta G_{\text{m}} = 0$ and we can write Equation (6).

$$\Delta G_{\text{m}} = \Delta H_{\text{m}} - T_{\text{m}} \Delta S_{\text{m}} = 0 \Rightarrow T_{\text{m}} = \frac{\Delta H_{\text{m}}}{\Delta S_{\text{m}}} = \frac{\Delta H_{\text{asso}}}{\Delta S_{\text{asso}}} \quad (6)$$

Introducing Equation (1) into Equation (6) yields Equation (7), in which the melting temperature can be simply deduced from the melting entropy (Figure 2b), a parameter

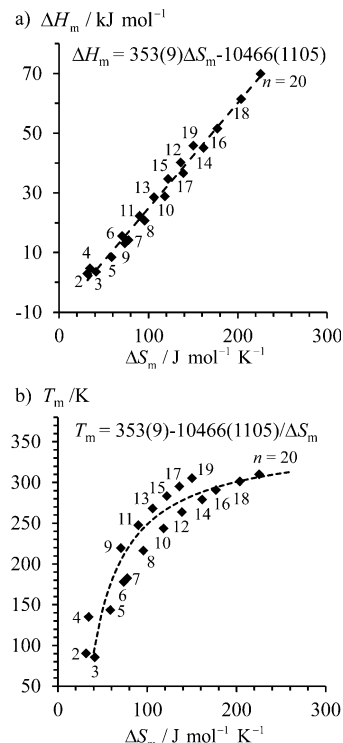


Figure 2. a) ΔH_{m} ($\text{C}_n\text{H}_{2n+2}$) versus ΔS_{m} ($\text{C}_n\text{H}_{2n+2}$) [Eq. (1)] and b) T_{m} versus ΔS_{m} ($\text{C}_n\text{H}_{2n+2}$) [Eq. (7)] correlation plots for the melting of saturated linear hydrocarbons $\text{C}_n\text{H}_{2n+2}$.^[19]

for which semi-empirical structure-based estimation schemes are available.^[20]

$$T_m = \alpha + \frac{\gamma}{\Delta S_{\text{asso}}} = \alpha - \frac{\gamma}{\Delta S_m} \quad (7)$$

We note here that the sign of the compensation free energy is crucial and $\gamma = 10.5(1.1) \text{ kJ mol}^{-1}$ found for the melting of linear alkanes induces larger melting temperatures when the melting entropies (hence the chain length) increase (Figure 2b). This trend is not general because decorrelation ($\gamma = 0$) was found, for instance, for the melting of silver *n*-alkanethiolate,^[21] whilst opposite decreases of T_m with increasing melting entropies ($\gamma < 0$) were reported for polycatenar complexes.^[22] Any predictive and rational correlation of the latter parameter with minor structural perturbations would bring an innovative tool for controlling melting temperatures within the frame of enthalpy–entropy compensation. However, melting enthalpies and entropies are collected at different temperatures for each compound (i.e., at T_m), and a common reference for comparing intermolecular cohesions within molecular solids is lacking. The closely related challenge of predicting boiling points was addressed by Hildebrand, who, taking Trouton's rule^[23] into account for the vaporization of liquids, introduced the concept of cohesive energy density $\text{ced} = (\Delta H_v - RT)/V_m$ for estimating the average cohesive force in a liquid (ΔH_v is the vaporization enthalpy and V_m is the molar volume).^[24] We suspect that this approach could be extended for melting processes, but the absence of Trouton's rule for solids requires the use of melting Gibbs free energy for estimating a cohesive free-energy density $\text{CFED} = -\Delta G_m^0/V_m$ along a homogeneous series of solid compounds at a common reference temperature. Considering the rodlike 4'-(dodecyloxy)-4-cyanobiphenyl compound **C12L**^{0,0} as a basic building block^[25] for which thermochemical data^[26] and intermolecular interactions^[27] have been carefully investigated, we explore here the structural and thermodynamic consequences of its systematic substitution with methyl groups in 4'-(dodecyloxy)-*i*'-methyl-*j*-methyl-4-cyanobiphenyl (**C12L**^{*f,j*}; Scheme 1). Particular efforts are made for obtaining coherent sets of melting enthalpies and entropies at a common reference temperature, a prerequisite

site for the exploitation of cohesive free-energy densities within the frame of enthalpy–entropy compensation.

Results and Discussion

Synthesis and structural characterization of methyl-substituted 4'-dodecyloxy-4-cyanobiphenyls **C12L^{*f,j*}:** The target compounds **C12L**^{*f,j*} are obtained following Suzuki–Miyaura strategies for the formation of the inter-aromatic C–C bond in **5**^{*f,j*},^[15,28,29] followed by Williamson etherifications (Scheme 1).^[30] The deleterious effect produced by a methyl group occupying the *ortho* position of the boronic esters **4**² leads to low yield for **5**^{2,2} and **5**^{3,2}, and only traces for **5**^{0,2}. This drawback forced us to synthesize the alternative 4-alkoxyphenyl boronic acid **7** for the preparation of acceptable quantities of **C12L**^{0,2} (Scheme 1, right). All compounds were purified by thorough column chromatography and gave satisfying elemental analyses, ¹H and ¹³C NMR spectra and adequate molecular peaks by using ESI-MS (see Experimental Section). Crystallization from hot methanol provided limited crops of X-ray quality prisms for all **C12L**^{*f,j*} compounds except for **C12L**^{0,3} and **C12L**^{2,2} (Table S1 and Figure S1, S2, Supporting Information).^[31] In line with the crystal structure reported for the non-methylated reference compound **C12L**^{0,0},^[25] the molecular structures of the monomethyl **C12L**^{3,0}, **C12L**^{2,0}, and **C12L**^{0,2} (Figure 3a) and dimethyl

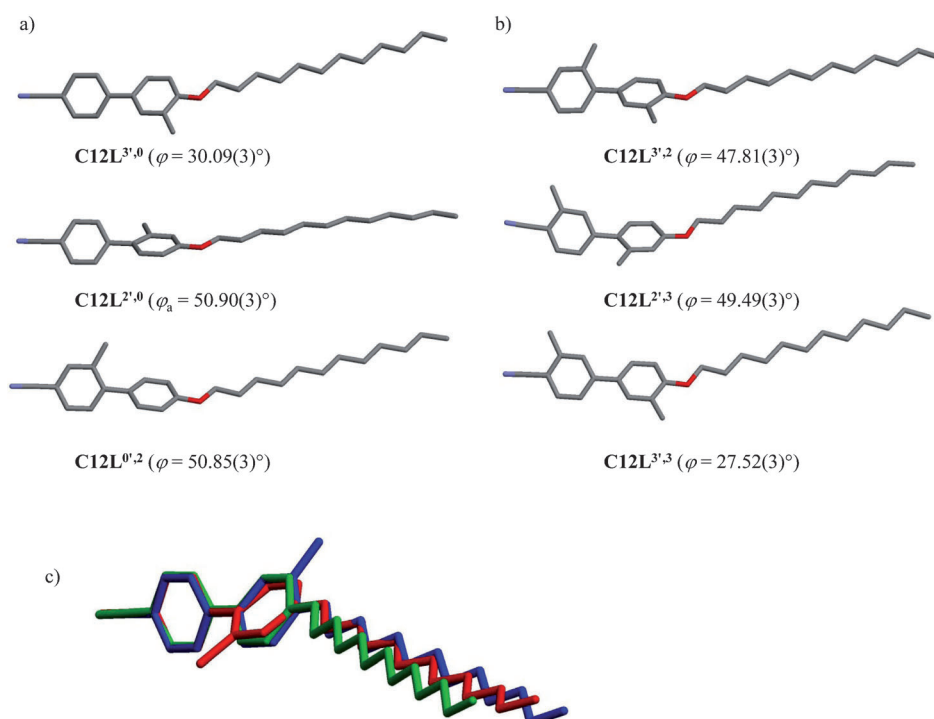
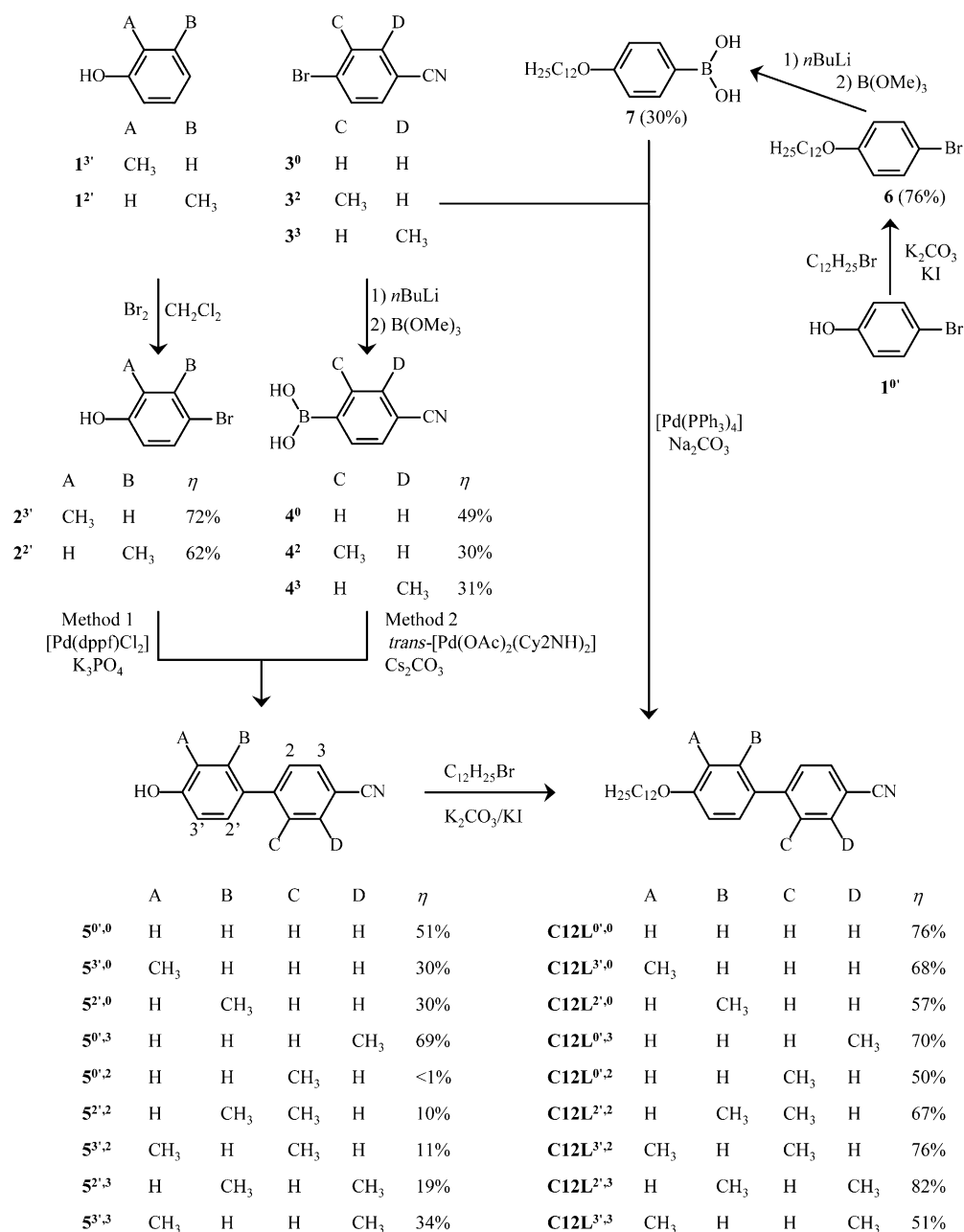


Figure 3. Molecular structures for a) monomethyl **C12L**^{3,0}, **C12L**^{2,0}, and **C12L**^{0,2}^[33] and b) dimethyl **C12L**^{3,2}, **C12L**^{2,3}, and **C12L**^{3,3} cyanobiphenyls. c) Superimposition of non-substituted **C12L**^{0,0} (green)^[25] and monomethyl substituted at the 3-position **C12L**^{3,0} (blue) and at the 2-position **C12L**^{2,0} (red) showing the increase of φ interplanar angles between the connected aromatic rings. Hydrogen atoms are omitted for clarity.



Scheme 1. Syntheses and chemical structures of the 4'-(dodecyloxy)-*i*'-methyl-*j*-methyl-4-cyanobiphenyl **C12L^{j,j}**. dppf = 1,10-Bis(diphenylphosphino)ferrocene and Cy₂NH = dicyclohexylamine.

C12L^{3,2}, **C12L^{2,3}**, and **C12L^{3,3}** (Figure 3b) cyanobiphenyls display variably twisted biaryl aromatic cores, to which planar all-*trans*-dodecyloxy chains are attached. The interaromatic twist angle φ is sensitive to the methyl groups bound to the 2- or 2'-positions, and it increases from $\varphi = 29.5(1.3)^\circ$ in **C12L^{0,0}**, **C12L^{3,0}**, and **C12L^{3,3}** (no methyl group in the 2- or 2'-positions) to $51.1(3.1)^\circ$ in **C12L^{2,0}**, **C12L^{0,2}**, **C12L^{3,2}**, and **C12L^{2,3}** (one methyl group in the 2- or 2'-positions, Figure 3c and Table S2).

All C–C, C–O, and C–N bond lengths are standard,^[32] leading to elongated rodlike molecules 2.56(2) nm long and 0.515(7) nm wide (Appendix 1, Table A1-1 in the Supporting

Information). In the crystal structures, each molecule is involved in several weak intermolecular C–H...N bonds,^[34] together with stronger sheared antiparallel CN...CN motifs (Table 1 and Appendix 2 in the Supporting Information).^[27] One immediately notices that methylation severely limits the latter processes, since four intermolecular CN...CN interactions are observed per **C12L^{0,0}** molecule, whilst only one related interaction per molecule could be identified for **C12L^{0,2}** and **C12L^{2,3}**, and none in the remaining compounds (Table 1). All crystallized **C12L^{j,j}** compounds display layered arrangements of the aromatic cyanobiphenyl units in the solid state and variable tilt angles with respect to the interfa-

Table 1. Number of intermolecular interactions^[a] and distances identified in the crystal structures of **C12L^{0,0}**, **C12L^{3,0}**, **C12L^{2,0}**, **C12L^{0,2}**, **C12L^{3,2}**, **C12L^{2,3}** and **C12L^{3,3}**.

	CN...CN <i>d</i> (C...N) [Å]	C _{arom} H...N <i>d</i> (C...N) [Å]	C _{aliph} H...N <i>d</i> (C...N) [Å]
C12L^{0,0}	4/3.5(1)	4/3.46(1)	0
C12L^{3,0}	0	2/3.560(2)	2/3.814(2)
C12L^{2,0}	0	6/3.48(3)	4/3.6(2)
	0	4/3.53(2)	2/3.575(2)
C12L^{0,2}	1/3.563(2)	6/3.58(4)	2/3.926(2)
C12L^{3,2}	0	4/3.7(2)	5/3.7(2)
C12L^{2,3}	1/3.441(2)	6/3.7(1)	4/3.8(1)
C12L^{3,3}	0	2/3.598(2)	2/3.700(2)

[a] C–H...N hydrogen bonds are considered for bond lengths *d*(H...N) < 3.0 Å and bond angles θ (C–H...N) > 120°. Antiparallel CN...CN interactions are considered for: *d*(C...N) ≤ 3.6 Å (see Appendix 2 in the Supporting Information).^[27] The number of interactions is given first followed by the bond length.

ces produced by the head-to-tail CN groups (Appendix 3 in the Supporting Information). We note that **C12L^{0,0}** is the only compound of the series for which the cyanobiphenyl cores lie perpendicular to the interface in the crystal, as found in its SmA mesophase at higher temperature.

Thermodynamic and structural characterization of the melting processes for methyl-substituted 4'-dodecyloxy-4-cyanobiphenyls **C12L^{i,j}:** In order to minimize deviations from thermodynamic equilibria, differential scanning calorimetric (DSC) traces were recorded at 0.5 K min^{−1} for compounds **C12L^{i,j}** and they showed single first-order melting processes transforming the room temperature solids into isotropic liquids (confirmed by polarized optical microscopy, Figure 4a and S3a–S9a, and Table 2), except for the reference compound **C12L^{0,0}**, which was known to display an intermediate smectic A mesophase prior to isotropization (Figure S10).^[26] The 8–15% decrease of the ratio between the molecular cross sections of the aliphatic chains and of the aromatic cores upon methylation $\delta = A_{\text{mol}}^{\text{tail}}/A_{\text{mol}}^{\text{core}}$ may partly explain the removal of any mesomorphism in the substituted cyanobiphenyls (Table A1,2 in Appendix 1 in the Supporting Infor-

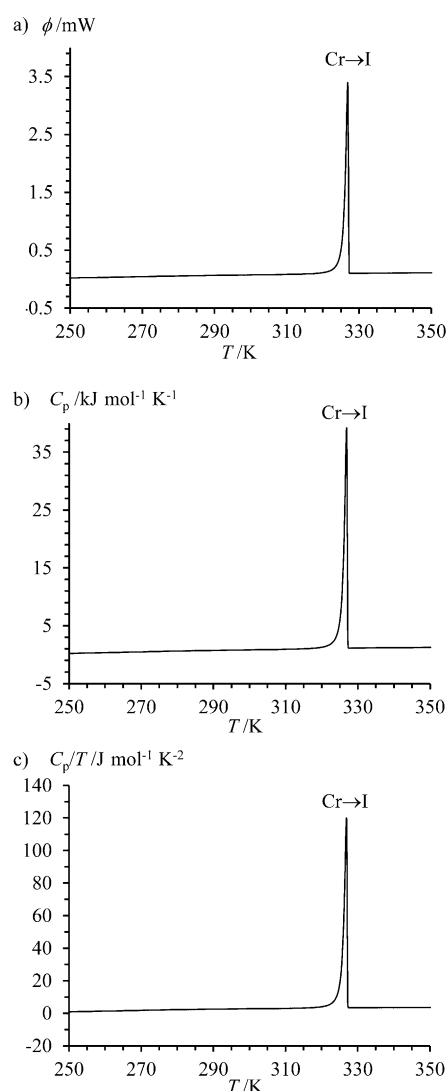


Figure 4. a) DSC trace recorded for the second heating of **C12L^{2,3}** and its transformation into b) molar heat capacity [Eq. (8)] and c) molar heat capacity per temperature unit.

Table 2. Thermodynamic parameters for the melting processes in **C12L^{i,j}**.^[a]

	Transitions ^[b]	ΔH_m [J mol ^{−1}]	ΔS_m [J mol ^{−1} K ^{−1}]	ΔG_m [kJ mol ^{−1}]	T_m ^[c] [K]	ΔH_m^0 [kJ mol ^{−1}]	ΔS_m^0 [J mol ^{−1} K ^{−1}]	ΔG_m^0 [kJ mol ^{−1}]	T_{dec} [K]
C12L^{0,0}	Cr→SmA	41.7(2)	122.2(6)	0.0(4)	341.6	38.8(1.7)	118.6(5.3)	3.4(3.2)	327.2(20.5)
	SmA→I	4.6(2)	12.6(6)	0.0(6)	362.2	6.2(7)	13.4(7)	2.2(9)	462.7(57.6)
	Cr→I ^[d]	46.3(4)	134.8(1.1)	0.0(8)	–	45.0(2)	132.0(6)	5.7(3.7)	340.9(21.7)
C12L^{3,0}	Cr→I	57.0(5)	167.1(1.5)	0.0(1.0)	341.2	45.8(8)	132.0(2.4)	6.5(1.5)	347.0(8.8)
C12L^{2,0}	Cr→I	32.5(2)	103.5(6)	0.0(4)	314.0	31.3(8)	99.6(2.5)	1.6(1.5)	314.3(11.3)
C12L^{0,3}	Cr→I	50.7(7)	155.4(2.2)	0.0(1.4)	326.6	43.9(7)	133.2(2.2)	4.2(1.3)	329.6(7.6)
C12L^{0,2}	Cr→I	55.4(1.0)	171.1(3.1)	0.0(2.0)	323.8	46.7(2)	143.0(7)	4.1(4)	326.6(2.1)
C12L^{2,2}	Cr→I	34.4(5.5)	111.9(17.9)	0.0(11.0)	307.8	39.7(1)	128.7(1)	1.4(2)	308.5(8)
C12L^{3,2}	Cr→I	54.0(7)	155.5(2.0)	0.0(1.4)	347.5	46.2(5)	130.9(1.5)	7.2(9)	352.9(5.6)
C12L^{2,3}	Cr→I	46.3(2)	142.0(6)	0.0(4)	325.7	43.2(3)	132.0(9)	3.9(6)	327.3(3.2)
C12L^{3,3}	Cr→I	44.1(7)	137.8(2.2)	0.0(1.5)	329.3	41.3(9)	128.4(3.0)	3.1(1.8)	321.7(10.3)

[a] The parameters marked with a 0 index correspond to standard values at 298 K, whereas all other data are given at the melting temperature T_m . [b] Cr = crystal, SmA = smectic A, I = isotropic liquid. [c] Melting temperature taken at the onset of the DSC trace. [d] Sum of the two successive phase transitions.

mation), while the resort to empirical Hildebrand solubility parameters attributes this phenomenon to the decrease in polarity produced by methylation of the cyanobiphenyl cores (Appendix 4 in the Supporting Information).^[35]

The energy flux $\phi = \Delta W / \Delta t$ measured by DSC at a constant scanning rate $v = \Delta T / \Delta t$ can be easily transformed 1) into molar constant pressure heat capacity C_p [Eq. (8) in which n is the number of moles, see also Figure 4b, Figures S3b–S10b in the Supporting Information] required for the determination of the melting enthalpies ΔH_m [Eq. (9), Figure 5, and Table 2 column 3] and 2) into temperature-normalized

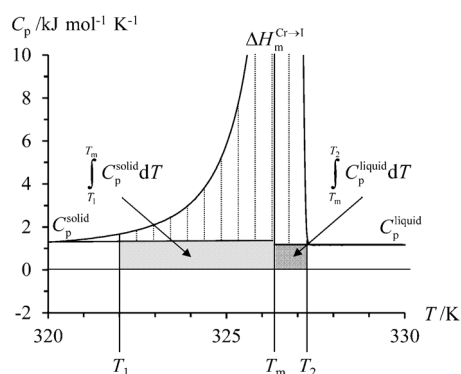


Figure 5. Molar heat capacity (C_p) trace recorded for **C12L^{2,3}** around its melting temperature with a graphical illustration of the method used for computing the thermodynamic melting enthalpy with Equation (9). T_1 , T_m , and T_2 are respectively the starting, melting, and end temperatures of the Cr→I phase transition.^[36]

malized molar heat capacity C_p/T (Figure 4c and Figures S3c–S10c in the Supporting Information) required for the calculations of melting entropies ΔS_m [Eq. (10), Table 2 column 4). Evidently, the free energy of melting $\Delta G_m = \Delta H_m - T_m \Delta S_m$ is zero for all compounds at their melting temperatures (Table 2 column 5).

$$\phi = \frac{\Delta W}{\Delta t} = \frac{n C_p \Delta T}{\Delta t} = n C_p v \Rightarrow C_p = \frac{\phi}{nv} \quad (8)$$

$$\Delta H_m = \int_{T_1}^{T_2} C_p dT - \int_{T_1}^{T_m} C_p^{\text{solid}} dT - \int_{T_m}^{T_2} C_p^{\text{liquid}} dT \quad (9)$$

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{T_1}^{T_m} \frac{C_p^{\text{solid}}}{T} dT - \int_{T_m}^{T_2} \frac{C_p^{\text{liquid}}}{T} dT \quad (10)$$

The minor change of the solid heat capacity below the melting temperature is reminiscent from the Dulong and Petit's law,^[37] and linear approximations of C_p versus T curves for both solid and liquid states are valuable approximations in this temperature range.^[38] Assuming that the linear correlation experimentally found for C_p^{liquid} versus T (Figure 5) also holds for the virtual liquid phase below its melting temperature, the associated Born–Haber cycle de-

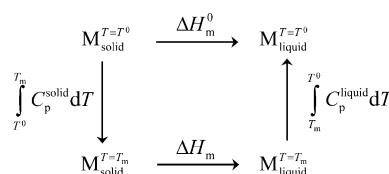


Figure 6. Born–Haber cycle used for estimating the standard enthalpy of melting in Equation (11).

picted in Figure 6 allows the estimation of “standard” melting enthalpies ΔH_m^0 [Eq. (11), Table 2 column 7] and entropies ΔS_m^0 [Eq. (12), Table 2 column 8] at a reference temperature T^0 (Appendix 5 in the Supporting Information).

$$\Delta H_m^0 = \Delta H_m + \int_{T^0}^{T_m} C_p^{\text{solid}} dT - \int_{T^0}^{T_m} C_p^{\text{liquid}} dT \quad (11)$$

$$= \int_{T^0}^{T_2} C_p dT - \int_{T^0}^{T_m} C_p^{\text{liquid}} dT$$

$$\Delta S_m = \Delta S_m + \int_{T^0}^{T_m} \frac{C_p^{\text{solid}}}{T} dT - \int_{T^0}^{T_m} \frac{C_p^{\text{liquid}}}{T} dT \quad (12)$$

$$= \int_{T^0}^{T_2} \frac{C_p}{T} dT - \int_{T^0}^{T_m} \frac{C_p^{\text{liquid}}}{T} dT$$

The resulting non-zero free energies of decohesion $\Delta G_m^0 = \Delta H_m^0 - T^0 \Delta S_m^0$ (Table 2, column 9) allow us to compare the trend for melting of the different compounds, whereas the associated temperatures of decohesion $T_{\text{dec}} = \Delta H_m^0 / \Delta S_m^0$ (Table 2 column 10) fix the points at which melting is expected if ΔH_m^0 and ΔS_m^0 are temperature independent. A rapid inspection of Table 2 shows that the “standard” thermodynamic melting parameters obtained for **C12L^j** do not drastically differ from those collected at variable melting temperatures (Figure S11 in the Supporting Information) and the concept of free energy of decohesion at a common reference temperature can be reasonably extended to $\Delta G_m^0 = \Delta H_m - T^0 \Delta S_m$ (Figure S12 in the Supporting Information). Interestingly, the existence of an intermediate mesophase, as found for **C12L^{0,0}**, is no more a drastic limiting factor for comparison purposes, since the corrected enthalpy and entropy changes accompanying the successive melting and isotropization processes are now referred to a common temperature and can be added to provide a global thermodynamic parameter estimating a single virtual solid→liquid process (Table 2). The broadening of the melting process at a low scan rate for **C12L^{3,3}** (Figure S9 in the Supporting Information) and even its splitting for **C12L^{2,0}** (Figure S4 in the Supporting Information) suggest the existence of polymorphism in the solid state as previously established for **C12L^{0,0}**.^[39] In our hands, the IR spectrum of solid **C12L^{0,0}** recorded in the 2200–2300 cm^{−1} range indeed showed the two separate bands of the C–N stretching vibrations as-

signed to the expected mixture between a minor thermodynamic form with $\nu(\text{CN})=2222\text{ cm}^{-1}$, and a major kinetic form with $\nu(\text{CN})=2231\text{ cm}^{-1}$ (Figure S13a in the Supporting Information).^[40] Upon melting, these two bands coalesce to give a single peak at $\nu(\text{CN})=2225\text{ cm}^{-1}$ in line with the removal any strong $\text{CN}\cdots\text{CN}$ interactions (Figure S13b in the Supporting Information).^[39,40] Reminiscent variable-temperature IR data can be collected for the melting of **C12L**^{*3',3*}, except that the thermodynamic form ($\nu(\text{CN})=2217\text{ cm}^{-1}$) represents the major polymorph for this compound in the solid state (Figure S14 in the Supporting Information).

Enthalpy–entropy compensation for the melting processes of methyl-substituted 4'-dodecyloxy-4-cyanobiphenyls **C12L^{*i,j*}:** The plot of ΔH_m^0 versus ΔS_m^0 for the solid to liquid melting processes is linear along the **C12L**^{*i,j*} series with a compensation temperature $\alpha=380(56)\text{ K}$ and a compensation free energy $\gamma=-6(7)\text{ kJ mol}^{-1}$ (Figure 7a). The same

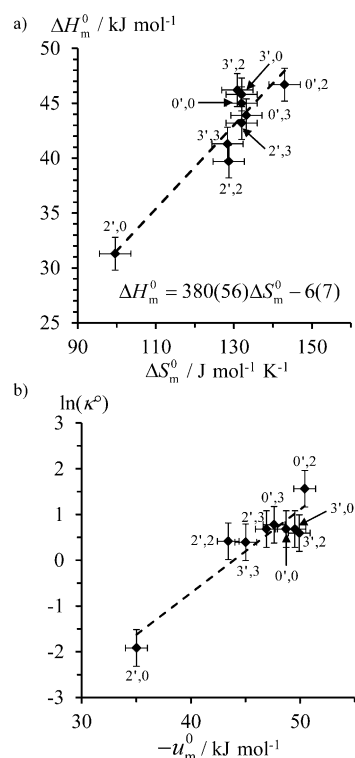


Figure 7. a) ΔH_m^0 versus ΔS_m^0 [Eq. (1)] and b) the logarithm of the force constants $\ln(\kappa^0)$ versus the potential well depth u_{\min}^0 for the melting of **C12L**^{*i,j*}.

enthalpy/entropy compensation (within experimental error) can be computed by using the thermodynamic parameters obtained at variable temperatures ($\Delta H_m=371(25)$ and $\Delta S_m-6(4)$, Figure S15 in the Supporting Information) and we conclude that the perturbations produced by methylation in **C12L**^{*i,j*} do not significantly affect the average minimum contact distance r_0 between the interacting entities in the solid state.

Interestingly, ΔH_m and ΔS_m values previously reported for **CnL**^{*n,0*} ($n=5-11$, Table S3)^[26] fit the trend found for **C12L**^{*i,j*}

and the linear H/S compensation also holds for change in chain length (Figure S15a in the Supporting Information). The logarithmic plot of the force constants κ^0 [computed with Eq. (3)] versus the attractive well depths u_{\min}^0 [computed with Eq. (2)] is evidently linear (Figure 7b and Figure S15b in the Supporting Information), but its interpretation within the frame of a single harmonic potential describing the intermolecular interactions in the solid state further requires the approximate Taylor series $\ln(\kappa^0) \approx \ln(\kappa_a^0) + [(\kappa^0 - \kappa_a^0)/\kappa_a^0]$ developed around an optimum central value κ_a^0 (Table S4).^[12,13] The large dispersion of the force constants κ^0 estimated at various melting temperature is not appropriate for this purpose (Figure S16a in the Supporting Information), and the more confined set of κ^0 computed at a common reference temperature (298 K) is better suited for being approximated by a straight line generated around $\kappa_a^0=1.70\text{ kN m}^{-1}$ (Figure S16b in the Supporting Information). Application of Equation (4) eventually gives $2^{1/6}r_0=1.3(2)\text{ Å}$ for the average optimum contact distance between the surface of the cyanobiphenyl entities (Figure S16c in the Supporting Information).

Within the regime of H/S compensation produced by methylation of the aromatic core or by chain extension in **CnL**^{*i,j*}, the combination of Equations (1) and (6) leads to Equations (13)–(15), in which the standard thermodynamic parameters depend on the compensation temperature (α), the compensation free energy (γ), and the decohesion temperatures (T_{dec}).

$$\Delta H_m^0 = \gamma \left(\frac{T_{\text{dec}}}{T_{\text{dec}} - \alpha} \right) \quad (13)$$

$$\Delta S_m^0 = \gamma \left(\frac{1}{T_{\text{dec}} - \alpha} \right) \quad (14)$$

$$\Delta G_m^0 = \gamma \left(\frac{T_{\text{dec}} - T^0}{T_{\text{dec}} - \alpha} \right) \quad (15)$$

Since the compensation free energy γ is close to zero within experimental error along the **C12L**^{*i,j*} series (Figure 7a), the decohesion or melting (Figures S17 and S18, respectively, in the Supporting Information) temperatures are only slightly influenced by the various thermodynamic parameters. Taking into account the molar volume $V_m = N_{\text{av}} \cdot V_{\text{mol}}$ estimated from the molecular volume (V_{mol}) computed for each **CnL**^{*i,j*} compound (N_{av} is Avogadro's number),^[41] we deduce the target standard cohesive free-energy densities $\text{CFED} = \Delta G_m^0 / V_m$ along the series (Table 3 and Table S5 in the Supporting Information). One immediately notices that CFED linearly increases with the decohesion temperature T_{dec} according to the empirical Equation (16) with $\lambda = -0.43(2)\text{ J K}^{-1}\text{ cm}^{-3}\text{ K}^{-1}$ and $\mu = 127(7)\text{ J cm}^{-3}$, an observation in line with the redundancy of these two parameters for estimating the trend of the molecules to interact in solid **C12L**^{*i,j*} (Figure 8a and Figure S19a in the Supporting Information).

Table 3. Molecular (V_{mol}) and molar volumes (V_{m}), standard free energy of decohesion (ΔG_{m}^0) and cohesive free-energy densities (CFED) in **C12L^{f,j}**.

Transitions ^[a]	$V_{\text{mol}}^{\text{[b]}}$ [Å ³]	$V_{\text{m}}^{\text{[c]}}$ [cm ³ mol ⁻¹]	$\Delta G_{\text{m}}^0^{\text{[d]}}$ [kJ mol ⁻¹]	CFED ^[e] [J cm ⁻³]
C12L^{f,0} Cr→I ^[f]	502.1	302.4	5.7(3.7)	-18.7(12.1)
C12L^{f,0} Cr→I	530.7	319.7	6.5(1.5)	-20.2(4.6)
C12L^{f,0} Cr→I	528.7	318.4	1.6(1.5)	-5.1(4.8)
C12L^{f,3} Cr→I	528.4	318.3	4.2(1.3)	-13.2(4.2)
C12L^{f,2} Cr→I	526.5	317.1	4.1(4)	-12.9(1.3)
C12L^{f,2} Cr→I	548.1	330.1	1.4(2)	-4.1(4)
C12L^{f,2} Cr→I	549.7	331.1	7.2(9)	-21.7(2.7)
C12L^{f,3} Cr→I	548.5	330.4	3.9(6)	-11.7(1.7)
C12L^{f,3} Cr→I	548.9	330.6	3.1(1.8)	-9.2(5.3)

[a] Cr = crystal, I = isotropic liquid. [b] Taken as the Connolly volume.^[41] [c] $V_{\text{m}} = N_{\text{av}} \times V_{\text{mol}}$ in which N_{av} is the Avogadro number. [d] $\Delta G_{\text{m}}^0 = \Delta H_{\text{m}}^0 - T^0 \Delta S_{\text{m}}^0$ is taken from Table 2 column 9. [e] $\text{CFED} = -\Delta G_{\text{m}}^0 / V_{\text{m}}$. [f] Sum of the two successive phase transitions leading to the isotropic liquid.

$$\text{CFED} = \frac{\Delta G_{\text{m}}^0}{V_{\text{m}}} = \lambda T_{\text{dec}} + \mu \quad (16)$$

The introduction of H/S compensation [Eq. (1)] together with $\Delta G_{\text{m}}^0 = \Delta H_{\text{m}}^0 - T^0 \Delta S_{\text{m}}^0$ and $T_{\text{dec}} = \Delta H_{\text{m}}^0 / \Delta S_{\text{m}}^0$ into Equation (16) eventually gives Equation (17), in which the melting entropy, measuring the degrees of freedom relaxed upon melting, (Figure 2b),^[44] can be deduced from the molar volume along the **CnL^{f,j}** series (Figure 8b and Figure S19b in the Supporting Information, domain of definition: $\Delta S_{\text{m}}^0 \neq -\gamma/(\alpha + \mu/\lambda)$).^[13]

$$V_{\text{m}} = \frac{(\Delta S_{\text{m}}^0)^2 (T^0 - \alpha) - \gamma \Delta S_{\text{m}}^0}{\Delta S_{\text{m}}^0 (\lambda \alpha + \mu) + \lambda \gamma} \quad (17)$$

Because of the very limited change in molar volumes induced by methylation in **C12L^{f,j}**, a satisfying fit with Equation (17) is difficult (Figure 8b), but the larger range of molar volumes explored with increasing chain length in **CnL^{f,j}** ($n=5-12$) improves the quality of the correlation (Figure S19b in the Supporting Information).

Conclusion

The minor perturbations of the intermolecular interactions induced by successive methylation in **C12L^{f,j}** can be caught by a single harmonic potential with an average intermolecular contact distance of 1.3(2) Å. According to Ford's approach,^[11-13] this situation leads to linear H/S compensation for the melting processes. Since the absolute melting temperatures of standard organic materials are globally close to that of the reference standard state (298 K), correcting enthalpies and entropies for temperature changes is not crucial and the usual assumption $\Delta H_{\text{m}}^0 \approx \Delta H_{\text{m}}$ and $\Delta S_{\text{m}}^0 \approx \Delta S_{\text{m}}$ is acceptable for extracting 1) average intermolecular contact distance r_0 in the solid state, 2) free energies of decohesion $\Delta G_{\text{m}}^0 = \Delta H_{\text{m}} - T^0 \Delta S_{\text{m}}$ at $T^0 = 298$ K, and 3) standard cohesion free-energy densities $\text{CFED} = -\Delta G_{\text{m}}^0 / V_{\text{m}}$. We have applied

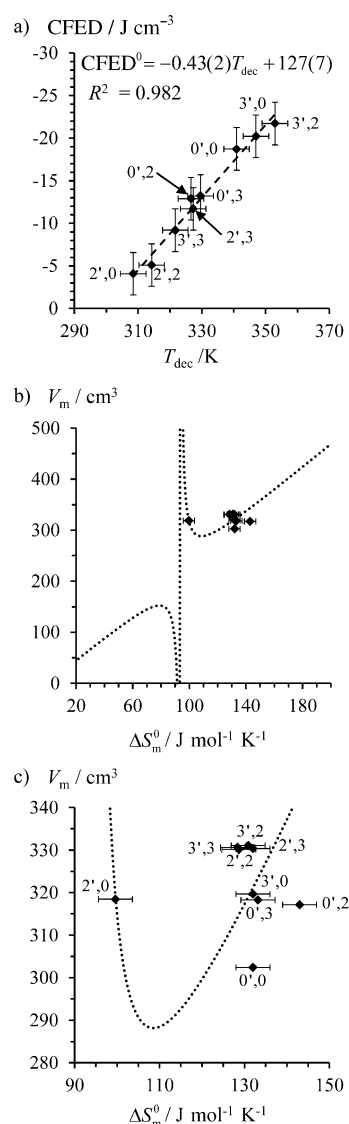


Figure 8. Plots of a) the standard cohesion free energy densities (CFED) versus the decohesion temperature (T_{dec}) and b) the molar volumes (V_{m}) versus ΔS_{m}^0 for **CnL^{f,j}**. The dotted trace shows the theoretical curve computed with Equation (17) and c) shows the assignment for each compound.

this approach for the melting of alkane $\text{C}_n\text{H}_{2n+2}$ of increasing length ($n=2-20$), for which H/S compensation is well established (Figure 2a). Firstly, the associated linear correlation established between the force constants and the potential well depth [Eqs. (2) and (3), and Figure S20a,b in the Supporting Information] yields an optimal contact distance of $2^{1/6}r_0 = 0.31(4)$ Å for the average optimum separation between the surface of the alkane entities [Eq. (4) and Figure S20c in the Supporting Information]. Secondly, the standard cohesion free energy densities (CFED) computed at 298 K are again linearly correlated with the melting temperatures (Figure 9a), and the relationship between the molar volumes and the melting entropies shown in Equation (17) allows simple predictions (Figure 9b). For instance, the molecular volume of $V_{\text{mol}} = 738$ Å³ computed for tetraco-

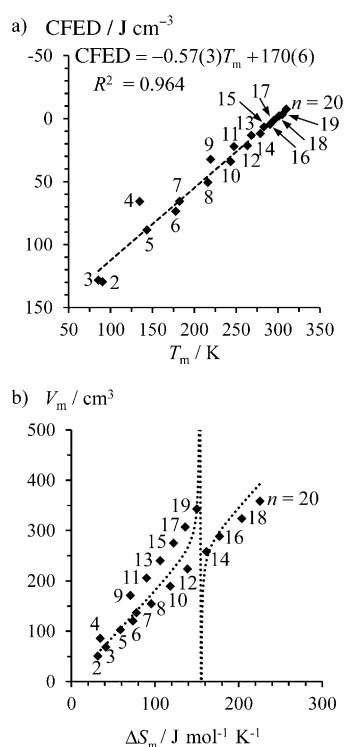


Figure 9. Plots of a) the cohesion free energy densities (CFED) versus the melting temperature (T_m) and b) the molar volumes (V_m) versus ΔS_m for saturated linear hydrocarbons C_nH_{2n+2} . The dotted trace shows the theoretical curve computed with Equation (17).

sane ($C_{24}H_{50}$)^[41] is translated into a molar volume of $V_m = 444.5 \text{ cm}^3 \text{ mol}^{-1}$, from which a molar entropy of $\Delta S_m = 254 \text{ J mol}^{-1} \text{ K}$ can be estimated with Equation (17). Equation (14) then provides the melting temperature $T_m = 312 \text{ K}$, whereas Equation (13) gives the melting enthalpy $\Delta H_m = 79.2 \text{ kJ mol}^{-1}$ in good agreement with experimental calorimetric results of $\Delta H_m = 81.75 \text{ kJ mol}^{-1}$, $\Delta S_m = 253.9 \text{ J mol}^{-1} \text{ K}$, and $T_m = 322 \text{ K}$.^[42] We are aware that multi-parameter predictions along the alkane series have numerous precedences,^[43] but the exploitation of the standard cohesion free energy densities (CFED) proposed in Equation (16) provides an unexpectedly simple and rational correlation between melting entropies and molecular volumes in Equation (17), which we believe to be useful for synthetic chemists in order to predict and tune melting temperatures beyond the limited predictions usually obtained with the exclusive resort of H/S compensation.^[13] Efforts are currently focussed on the extension of the CFED concept for the rationalization and prediction of the successive melting processes characterizing the transformation of solids into liquid crystals and of liquid crystals into isotropic liquids.

Experimental Section

Solvents and starting materials: These were purchased from Strem, Acros, Fluka AG and Aldrich and used without further purification unless otherwise stated. Compounds **4**⁰,^[44] **42**,^[45] **5**^{2,0},^[15] and **5**^{2,2}^[15] were

prepared according to literature procedures. The synthesis of **22**⁰, **23**⁰, **4**³, **5**^{0,0}, **5**^{3,0}, **5**^{3,2}, **5**^{0,3}, **5**^{2,3}, **5**^{3,3}, **6**, **7**, **C12L**^{0,0}, **C12L**^{3,0}, **C12L**^{0,2}, **C12L**^{0,3}, **C12L**^{2,2}, **C12L**^{3,2}, **C12L**^{2,3}, **C12L**^{3,3} and **C12L**^{0,2} are given in Appendix 6 (Supporting information). Acetonitrile and dichloromethane were distilled over calcium hydride. Silicagel plates Merck 60 F254 were used for thin layer chromatography (TLC) and Fluka silica gel 60 (0.04–0.063 mm) or Acros neutral activated alumina (0.050–0.200 mm) was used for preparative column chromatography.

Spectroscopic and analytical measurements: ¹H and ¹³C NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer. Chemical shifts are given in ppm with respect to TMS. Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10⁻⁴ M solutions on an Applied Biosystems API 150EX LC/MS System equipped with a Turbo Ion spray source. Elemental analyses were performed by K. L. Buchwalder from the Microchemical Laboratory of the University of Geneva. TGA were performed with a thermogravimetric balance Mettler Toledo Star Systems (under N₂). DSC traces were obtained with a Mettler Toledo DSC1 Star Systems differential scanning calorimeters from 3–5 mg samples (5 and 0.5 °C min⁻¹, under N₂). The characterization of the mesophases and of the isotropic liquids were performed with a polarizing microscope Leitz Orthoplan-Pol with a Leitz LL 20x/0.40 polarizing lens, and equipped with a Linkam THMS 600 variable-temperature stage. The variable-temperature FT-IR spectra were recorded on an IRTF Nicolet iS10 spectrometer in diffuse reflectance mode by using a high-temperature diffuse reflectance environmental chamber. The samples were diluted into a KBr matrix and the resulting mixtures containing about 10% of compound were ground before being heated at 200 °C during few minutes. After cooling to room temperature the FT-IR spectra were recorded in the 20–200 °C and in the 200–20 °C temperature ranges using a heating or cooling rate of 2 °C min⁻¹. The spectra were recorded with a resolution of 0.4 cm⁻¹. The mathematical analyses were performed by using Igor Pro (WaveMetrics Inc.) and Excel (Microsoft) softwares.

X-ray crystallography: A summary of crystal data, intensity measurements and structure refinements for **C12L**^{3,0}, **C12L**^{2,0}, **C12L**^{0,2}, **C12L**^{3,2}, **C12L**^{2,3} and **C12L**^{3,3} is given in Table S1 (Supporting Information). All crystals were mounted on quartz fibers with protection oil. Cell dimensions and intensities were measured at 180–200 K on an Agilent Supernova diffractometer with mirror-monochromated CuK α radiation ($\lambda = 1.54187 \text{ \AA}$) and CCD camera. Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods (SIR97),^[46] all other calculation were performed with SHELXL^[47] systems and ORTEP^[48] programs. CCDC-917848 (**C12L**^{3,0}), CCDC-917849 (**C12L**^{2,0}), CCDC-917850 (**C12L**^{0,2}), CCDC-917851 (**C12L**^{3,2}), CCDC-917852 (**C12L**^{2,3}), and CCDC-917853 (**C12L**^{3,3}) the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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