Smectic polymorphism and melting processes of molecules in the case of 4,4'-di(p,n-alcoxybenzylideneamino) biphenyls

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SMECTIC POLYMORPHISM AND MELTING PROCESSES OF MOLECULES IN THE CASE OF 4,4'-di(*p,n*-ALCOXYBENZYLIDENE-AMINO) BIPHENYLS

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Résumé. — L'analyse des résultats expérimentaux obtenus par l'étude volumétrique de la série des 4,4'-di(*p,n* alkoxybenzylidèneamino) diphényles nous a permis de calculer, pour la phase cristalline et les 3 phases smectiques, les volumes molaires des parties aromatique et aliphatique des molécules en fonction de la température. Les chaînes paraffiniques fondent en une seule étape à la transition faisant passer l'échantillon de la phase cristalline à la première phase smectique. Le degré d'ordre dans les couches aromatiques décroît par étapes successives d'une phase mésomorphe à la suivante.

Abstract. — By analyzing the experimental data obtained in a volumetric study of the 4,4'-di(*p,n* alcoxybenzylideneamino) biphenyl series, we have calculated the molar volume of the aromatic and aliphatic parts of the molecules as a function of temperature. The aliphatic chains melt in a single step at the transition from the crystal to the first smectic phase. The degree of disorder in the aromatic layers increases stepwise from one polymorphic phase to the next.

1. Introduction. — In a previous paper [1], we studied the temperature dependence of the volume of the $n = 18$ term of the 4,4'-di(*p,n*-alcoxybenzylideneamino) biphenyl homologous series of smectogens :

$$C_nH_{2n+1}O—\varnothing—CH=N—\varnothing—\varnothing—N=$$

$$=CH—\varnothing—OC_nH_{2n+1} .$$

From the magnitude of the volume change observed at the crystal → smectic transition we deduced that the occurrence of the thermotropic mesomorphic phases is directly related to the melting of the paraffin tails of the molecules. An ESR study [2] has shown that aliphatic chains are disorganized in the smectic state. In a further study [3], by combining volume measurements with those of low-angle X-ray diffraction we were able to show the predominant rôle played by the *liquid* paraffin chains in the smectic organization and in the tilt of the molecules within the layers.

In this paper, we would like (i) to give a more detailed volumetric proof of the melting of the paraffin tails at the crystal → smectic transition, (ii) to show that this phenomenon occurs not only when the paraffin tails are sufficiently long, but even when they contain as few as 4 carbon atoms, and (iii) to analyze the melting process of the aromatic stems of the molecules.

2. Experimental. — Using dilatometry [1], we have studied systematically the temperature dependence of the volume of all the even terms, from $n = 4$ up to $n = 18$, of the 4.4'-di(*p,n*-alcoxybenzylideneamino) biphenyl homologous series mentioned above. The experimental procedure along with the experimental data will be described in detail in a separate paper [4]. However, for the sake of clarity, it is convenient to note here the following features.

The polymorphic transitions are characterized by a rapid increase of the volume within a narrow temperature range. Apart from the crystal C observed at room temperature, the isotropic liquid or eventually a nematic phase observed at high temperatures ($T \sim 300$ °C), all the terms of the series that we have considered show on heating 3 smectic phases successively specified by S_1, S_2 and S_3. Each of these is of the same type whatever the length of the molecules. Within the limits of temperature stability of each phase the volume increases linearly with temperature (Fig. 1). For a given phase, the thermal expansion coefficient of the molar volume depends linearly on the number n of carbon atoms of the aliphatic chain (Fig. 2). Finally, for a given phase, at a given temperature, the molar volume increases linearly with n (Fig. 3).
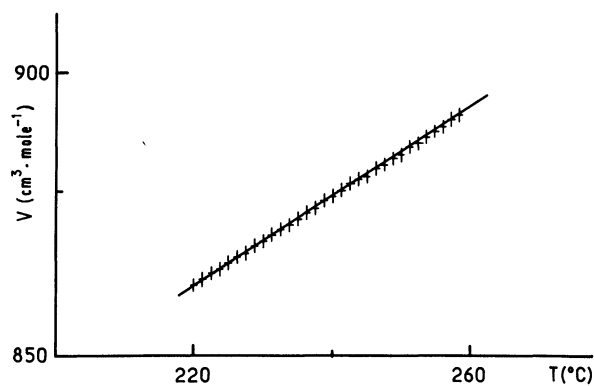
FIG. 1. — Molar volume of the $n = 14$ term of the series in smectic S_3 phase as a function of temperature.
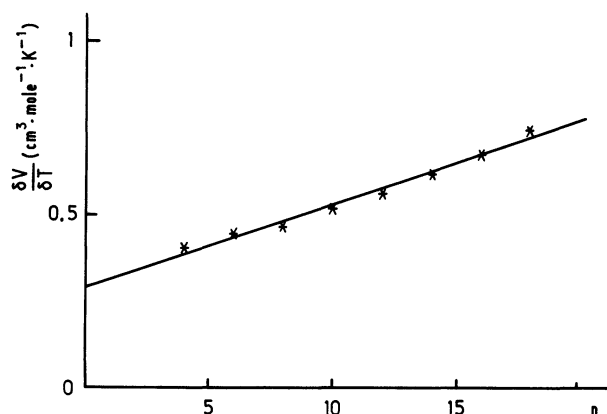

FIG. 2. — Thermal expansion coefficient of the molar volume in phase S_2 as a function of the number n of carbon atoms,
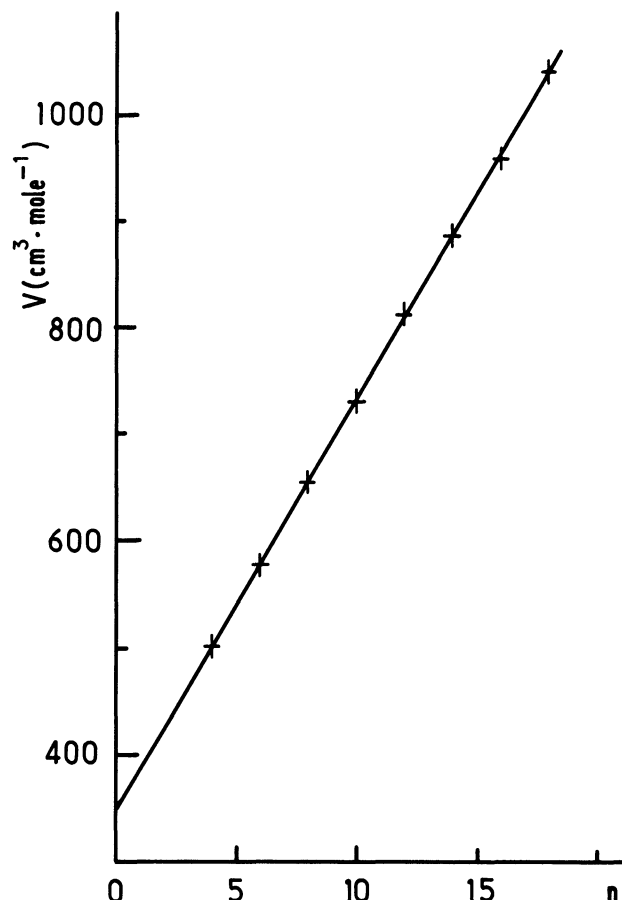

FIG. 3. — Molar volume in phase S_3 at 250 °C as a function of the number n of carbon atoms.

3. **Interpretation of results.** — These volumetric observations are all consistent with the assumption of additivity of the partial molar volumes of the constituents of the molecules. To a first approximation, the central aromatic stem and the paraffin tails seem to act fairly independently from one another, at least as far as their volume is concerned. Mathematically, one can write :

$$V(n, T) = V_a(T) + 2 nV_p(T)$$

$$V_a(T) = V_a(0) + T\frac{\partial V_a}{\partial T}$$

$$V_p(T) = V_p(0) + T\frac{\partial V_p}{\partial T}$$

where $V(n, T)$ stands for the molar volume of the nth term of the series, $V_a(T)$ and $V_p(T)$ respectively for the molar volume of the aromatic part of the molecules ($n = 0$) and of one methylene group, and $\partial V_a/\partial T$ and $\partial V_p/\partial T$ for the corresponding thermal expansion coefficients. To fully describe the volumetric behaviour of the system, it suffices therefore to know the value of 4 parameters for every phase, namely $V_a(0)$, $V_p(0)$, $\partial V_a/\partial T$ and $\partial V_p/\partial T$.

From our experimental data [4], that is from some 600 measurements of $V(n, T)$ as a function of n and T,

and by applying a least-square linear regression analysis, we have calculated the value of these 4 parameters for the crystal C and the 3 smectic phases S_1, S_2, S_3 (Table I). To do this, we have proceeded in three steps. We have, first, determined the analytical expression giving $V(n, T)$ as a function of T for every polymorphic phase of all the terms of the series of smectogens that we have considered. We have then analyzed the linear dependence of $V(n, T)$ upon n at constant temperature, and calculated in each phase the values of $V_a(T)$ and $V_p(T)$ at various temperatures.

TABLE I

Molar volumes, $V_a(0)$ and $V_p(0)$, at 0 °C of the aromatic stem of the molecules and of one methylene group (in $cm^3.mole^{-1}$), and corresponding thermal expansion coefficients, $\partial V_a/\partial T$ and $\partial V_p/\partial T$ (in $cm^3.mole^{-1}.K^{-1}$), for the crystal C and the 3 smectic phases S_1, S_2, S_3.

	$V_a(0)$	$V_p(0)$	$\frac{\partial V_a}{\partial T} \times 10$	$\frac{\partial V_p}{\partial T} \times 10^3$
	—	—	—	—
C	315.8	14.73	1.03	1.58
S_1	288.8	15.57	2.05	13.5
S_2	271.6	15.98	2.93	11.9
S_3	240.9	15.97	4.28	12.9

Finally, by considering the thermal evolution of these volumes, we have deduced the thermal expansion coefficients $\partial V_a/\partial T$ and $\partial V_p/\partial T$. We estimate the standard error to be of the order of 1 %.

4. Discussion. — To study separately the thermal behaviour of the paraffin and the aromatic parts of the molecules during the process of smectic polymorphism we have calculated from table I the values of $V_p(T)$ and $V_a(T)$ as a function of T. Figures 4 and 5 illustrate the results that we have obtained. The limits of temperature stability of each phase have arbitrarily been chosen to correspond to those of the $n = 14$ term of the series. Although the transition temperatures depend noticeably on the number n of carbon atoms, the following conclusions remain nevertheless significantly the same for the whole series, whatever the actual length of the paraffin tails.
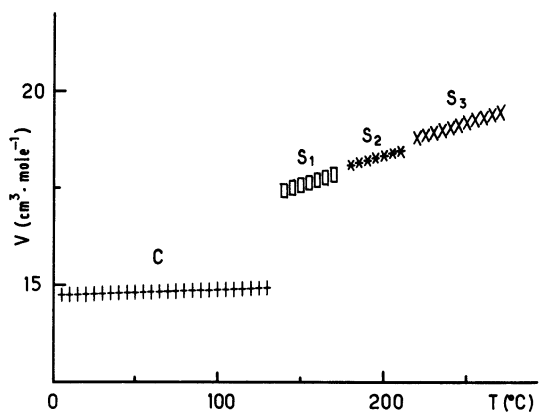
FIG. 4. — Molar volume of one methylene group as a function of temperature.
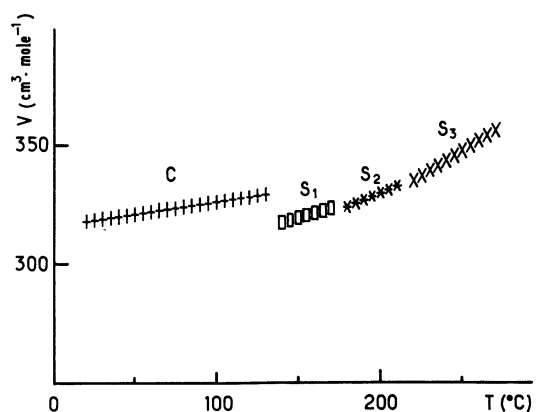
FIG. 5. — Molar volume of the aromatic stems as a function of temperature.

Let us, first, consider the behaviour of the aliphatic parts of the molecules. From figure 4, it is clear that the molar volume of the methylene groups undergoes a sudden and important increase as the temperature goes beyond 137.5 °C, the transition temperature corresponding to the onset of the mesomorphic state. The same is true for the thermal expansion coefficient. The magnitudes of

the volume change observed ($\sim$ 15 %) and of the variation of the thermal expansion coefficient (which changes from 1.5×10^{-3} cm^3.mole^{-1}.K^{-1} to 13.5×10^{-3} cm^3.mole^{-1}.K^{-1}) are in agreement with what we know of the melting of paraffins or of crystalline polymers. These results clearly indicate that at the $C \rightarrow S_1$ transition the paraffin tails of the molecules become disorganized. For the next polymorphic transitions observed, that are $S_1 \rightarrow S_2$ and $S_2 \rightarrow S_3$, the changes of molar volume as well as of the thermal expansion coefficients are negligible within the experimental error. Once molten at the $C \rightarrow S_1$ transition, the paraffin tails seem to undergo only minor changes in their organization and in their compactness in space. It is worth stressing here that these conclusions are valid for all the terms of the series we have considered in this work. At a given temperature, regardless of whether this has been chosen in the range of thermal stability of the crystal or of one of the mesomorphic phases, the molar volume $V(n, T)$ varies perfectly linearly with n from $n = 4$ up to $n = 18$.

Let us consider now the behaviour of the aromatic stems. Unlike the case of the paraffinic tails, where the melting proceeds in one single step, the fusion of the aromatic parts of the molecules takes place in as many distinct steps as there are polymorphic transition : the thermal expansion coefficient steadily increases with temperature from one polymorphic phase to the next (Table I). Each step corresponds to an increase of the degree of disorder of the system.

This is supported by the wide-angle X-ray diffraction diagrams that we have recorded (Fig. 6). The crystal C is characterized by a large number of rather sharp peaks indicating a three-dimensional periodical arrangement of the molecules. The smectic S_1 is characterized by an X-ray pattern containing one narrow peak and one rather large band; the latter suggests that some disorganization occurred in the aromatic layers. For the smectic S_2, only one narrow peak is observed which is consistent with the well-known two-dimensional hexagonal arrangement of the molecules in the smectic layers; presumably, the molecules gain still more disorder, being capable of orienting themselves randomly around their axis of elongation. As for the last smectic phase, S_3, the single
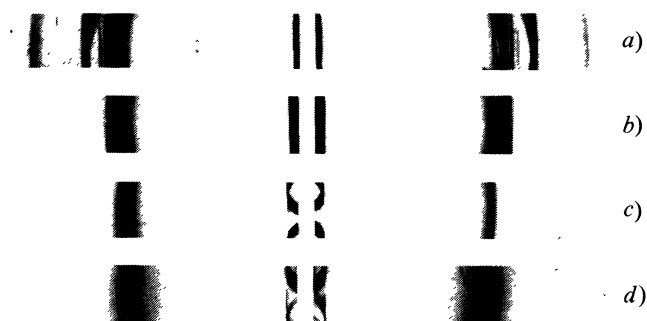

FIG. 6. — Wide-angle X-ray diffraction patterns : a) crystal, b) S_1, c) S_2, d) S_3.

diffuse band that is observed is evidence of the liquid like arrangement of the molecules within the aromatic layers.

The question arises, now, of whether the stepwise disorganization of the aromatic stems results also in a discontinuous increase of their molar volume.

Quite unexpectedly, instead of increasing at the first transition, that is at the transition from the crystal to the smectic phase, the volume of the aromatic stems decreases sharply, beyond any possible experimental error, by about 3 % (Fig. 5). This phenomenon, similar in some ways to the fusion of ice, is confirmed by a dilatometric study of the kinetics of the reverse transition : $S_1 \rightarrow C$ [4]. After it has decreased by a quantity corresponding to the crystallization of the paraffin tails, the volume of the sample again increases perceptibly, indicating the participation of the aromatic stems in an expansional process of organization. Presumably, the aromatic stems have to make the best of the structure that has been imposed upon the whole by the paraffin tails which have crystallized first.

The transitions from S_1 to S_2, then to S_3, are quite normal; the molar volume increases stepwise with the degree of disorder in the aromatic layers. However, owing to the insufficient accuracy ($\sim 1 \%$) to which $V_a(0)$ is determined for each polymorphic phase, the very small volume changes ($\sim 1\text{-}2 \%$) induced by the transitions cannot be accurately determined from figure 5. To see them better, and also to evaluate their magnitude, one has to come back to the original experimental curves [4] giving $V(n, T)$ as a function of T for different values of n. It is very easy indeed to measure from these curves the change ΔV of the molar volume of the samples at any transition from one phase to the next (Table II). Although the accuracy of such an evaluation is not very high ($\sim 0.5 \text{ cm}^3.\text{mole}^{-1}$), it is possible however to make two observations. Firstly, at the $S_2 \rightarrow S_3$ transition the volume increases

TABLE II

Molar volume increments $\Delta V_{S1 \rightarrow S2}$ *and* $\Delta V_{S2 \rightarrow S3}$ *(in* $cm^3.mole^{-1}$*) registered as a function of the number n of carbon atoms at the transition temperatures* $T_{S1 \rightarrow S2}$ *and* $T_{S2 \rightarrow S3}$ *(in* °C*).*

n	$T_{S1 \rightarrow S2}$	$\Delta V_{S1 \rightarrow S2}$	$T_{S2 \rightarrow S3}$	$\Delta V_{S2 \rightarrow S3}$
4	235.5	6.1	253.0	7.2
6	214.0	3.3	249.5	4.7
8	204.0	2.7	244.0	5.6
10	193.0	2.5	233.0	5.8
12	186.0	1.9	226.0	5.0
14	177.0	1.7	215.0	5.5
16	176.5	1.9	211.0	4.6
18	172.0	1.1	205.0	5.5

by a quantity ($\sim 5.5 \text{ cm}^3.\text{mole}^{-1}$) which is independent of the length of the paraffin chains. Apparently it reflects the expansion of only the aromatic stems, the aliphatic tails not changing their specific volume. On the other hand, the situation is a little more complicated at the $S_1 \rightarrow S_2$ transition. The molar volume increment ΔV decreases as the length of the aliphatic chains increases, especially for the lower terms of the series ($n < 8$). Presumably, the bulkier the paraffin tail, the more disorganized the aromatic stems in phase S_1 (but this is a matter of 1 % change on V_a). The wide-angle X-ray diffraction diagrams that we have recorded for S_1 (Fig. 6) support this idea ; the width of the diffuse band near the narrow diffraction peak increases noticeably with the molecular weight of the sample.

In conclusion, the occurrence of the smectic phases from the crystal seems to be connected with the melting of only the aliphatic parts of the molecules, while the smectic polymorphism itself seems to be related to the stepwise increase of the degree of disorder in the aromatic layers.

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