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Dibenzotetraaza[14]annulene Complexes. Part 2: Mesomorphic Properties of Four Chain Substituted Compounds

S. Forget [a] & M. Veber [a]
[a] Laboratoire de Physique des Solides, Université Paris-Sud, Centre Universitaire, Băt. 570, 91405, ORSAY Cedex, France

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Dibenzotetraaza[14]annulene Complexes. Part 2[†]: Mesomorphic Properties of Four Chain Substituted Compounds

S. FORGET and M. VEBER*

*Laboratoire de Physique des Solides, Université Paris-Sud,
Centre Universitaire, Bât.510, 91405 ORSAY Cedex, France*

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The mesomorphic properties of dibenzotetraaza[14]annulene complexes and ligands bearing four alkoxy chains are described. They were investigated by microscopic observations, DSC experiments and X-Ray diffraction studies. All the compounds, even the short chains homologues, exhibit wide range hexagonal columnar phases.

Keywords: Metallomesogens; liquid crystals; x-ray; dibenzotetraaza[14]annulenes

1. INTRODUCTION

Few series of non-saturated tetraazamacrocyclic complexes are described to exhibit liquid crystal properties. To our best knowledge, only phthalocyanine and porphyrin derivatives have been described to exhibit D_h and nematic phases [1,2,3,4,5,6,7]. We have published recently the synthesis of dibenzotetraaza[14]annulene derivatives $\underline{1}$ substituted by four paraffinic chains [8]. We have also synthesised some ligands to compare their properties with those of the corresponding complexes. Some preliminary results concerning the mesomorphic properties of such compounds were given. The

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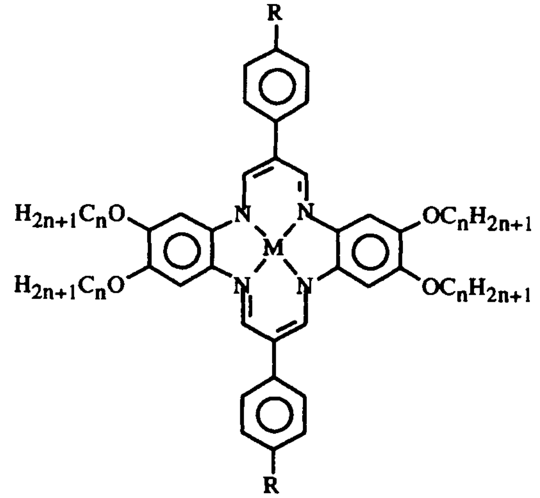
[†] Part 1: S. Forget, M. Veber and H. Strzelecka, *Mol. Cryst. Liq. Cryst.*, **258**, 263 (1995).

*To whom correspondence should be addressed.

aim of this paper is to describe further results concerning the studies of liquid crystal behaviours of compounds 1 and some corresponding ligands.



n = 4, 6, 7, 8, 9, 10, 11, 12; M = Ni; R = H
n = 12; M = Ni; R = Br
n = 12; M = H_2; R = H

1

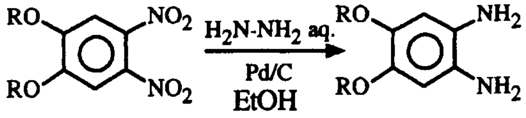
SCHEME 1

The general formula of the complexes studied as well as the ligands is given below:

The notation used to name the compounds is as follows: **XCn**, *X* representing the number of paraffinic chains grafted on the macrocycle and *n*, the number of carbon atoms per aliphatic chain. So, the compound bearing four dodecyloxy chains will be the **4C12** complex and the compound containing two bromine atoms: **4C12Br**. A'' will be added for the ligand.

2. SYNTHESIS

The synthesis of the complexes was described elsewere [9]. Nevertheless, some modifications can be introduced. The free 4,5-dialkoxy-1,2-phenylenediamines were obtained by direct reduction of the corresponding dinitro compounds (synthesized in one step under biphasic conditions) [9] according to:



SCHEME 2

Such amines are stable enough to be stored under inert atmosphere at 5°C. They were used, freshly prepared, to obtain the desired dibenzotetraaza[14]annulene complexes by the same template reaction as in reference [9].

The mesomorphic properties of the whole series and of the ligand were studied by microscopic observations under polarised light, DSC and X-Ray diffraction. They are presented below.

3. MICROSCOPIC OBSERVATIONS AND DSC

3.1. Complexes

Microscopic observations were performed with a Leitz Orthoplan polarized microscope equipped with a Mettler FP5 variable temperature stage. Transition temperatures and enthalpies were determined with a DSC7 Perkin Elmer apparatus.

The transition temperatures and enthalpies are given in Table I. Due to the high clearing temperatures, some care was taken to avoid some decomposition of the sample during the microscopic observations and DSC measurements: all were performed without reaching the clearing temperatures. Characteristic textures are generally obtained by slow cooling of the sample from the isotropic phase, in this case we have chosen a different method consisting of the slow evaporation of a solvent [8] in the mesophase. Due to the presence of the solvent (dichloromethane or toluene) the compound has the mobility to rearrange and form typical textures. Some of them are given in Plates 1 to 3. They show the growth of some hexagons in the isotropic phase during the evaporation of the solvent (toluene) in the case of the **4C6** complex. During the evaporation, some fanshapes appear on the sides of the hexagonal monodomains. Such behaviour is characteristic of columnar hexagonal phases. Concerning the **4C4** complex, no typical textures were ever obtained, due to the high transition temperatures where some decomposition occurs. Nevertheless, on heating a pure sample from

TABLE I Transition temperatures and enthalpies for the dibenzotetraaza[14] annulene complexes and the **4C12′** ligand

Compounds	*Transition temperatures (°C)* *(Transition enthalpies (J/g))*
4C4	$\mathrm{Cr} \underset{207(9.4)}{\overset{239(9.7)}{\rightleftharpoons}} \mathrm{M} \underset{256(1.2)}{\overset{267(2.2)}{\rightleftharpoons}} \mathrm{M} \xrightarrow{>300} \mathrm{I}^*$
4C6	$\mathrm{Cr} \underset{139(16)}{\overset{161(16.8)}{\rightleftharpoons}} \mathrm{D_h} \xrightarrow{360.6} \mathrm{I}^*$
4C7	$\mathrm{Cr} \underset{95(14.0)}{\overset{136(15.3)}{\rightleftharpoons}} \mathrm{D_h} \xrightarrow{>300} \mathrm{I}^*$
4C8	$\mathrm{Cr} \underset{41(5.3)}{\overset{112(13)}{\rightleftharpoons}} \mathrm{D_h} \xrightarrow{349.5} \mathrm{I}^*$
4C9	$\mathrm{Cr_1} \underset{25(3.3)}{\overset{27.6(6.6)}{\rightleftharpoons}} \mathrm{Cr_2} \xrightarrow{60.1(8.8)} \mathrm{Cr_3} \xrightarrow{111(3.0)} \mathrm{D_h} \xrightarrow{340.5} \mathrm{I}^*$ $\mathrm{Cr_2} \xleftarrow[48.9(8.7)]{} \mathrm{D_h}$
4C10	$\mathrm{Cr_1} \xrightarrow{60(0.18)} \mathrm{Cr_2} \xrightarrow{107(16.9)} \mathrm{D_h} \xrightarrow{340} \mathrm{I}^*$ $\mathrm{Cr_1} \xleftarrow[53(10.7)]{} \mathrm{D_h}$
4C11	$\mathrm{Cr_1} \xrightarrow{46(39.5)} \mathrm{Cr_2} \xrightarrow{102.6(15.4)} \mathrm{D_h} \xrightarrow{336} \mathrm{I}^*$ $\mathrm{Cr_1} \xleftarrow[21.1(14.5)]{} \mathrm{Cr} \xleftarrow[30.1(6.1)]{} \mathrm{D_h}$
4C12	$\mathrm{Cr_1} \xrightarrow{46(32.0)} \mathrm{Cr_2} \xrightarrow{99(9.4)} \mathrm{D_h} \xrightarrow{332} \mathrm{I}^*$ $\mathrm{Cr_1} \xleftarrow[27(31.6)]{} \mathrm{D_h}$
4C12Br	$\mathrm{Cr_1} \xrightarrow{22(25.7)} \mathrm{Cr_2} \xrightarrow{87(1.8)} \mathrm{D_h} \xrightarrow{358} \mathrm{I}^*$ $\mathrm{Cr_1} \xleftarrow[4(25.7)]{} \mathrm{D_h}$
4C12′	$\mathrm{Cr} \underset{73.1(15.7)}{\overset{96.8(16.9)}{\rightleftharpoons}} \mathrm{D_h} \overset{209.2}{\rightleftharpoons} \mathrm{I}$

*Partial or total decomposition of the sample.

room temperature to its clearing point (>300°C), the complex, very dark in the beginning of the observation becomes lighter, birefringent and more or less fluid around 239°C.

PLATE 1 Compound **4C6**, $T = 90°C$ (Toluene). (See Color Plate XII).

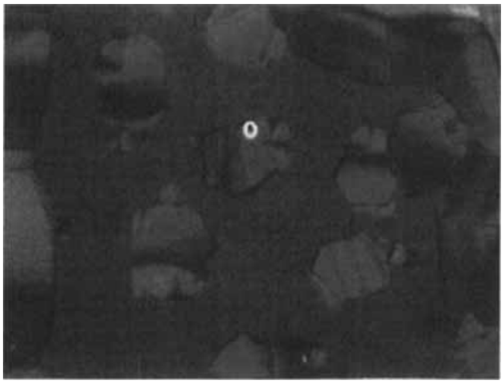


PLATE 2 Compound **4C6**, $T = 90°C$ (Toluene). (See Color Plate XIII).

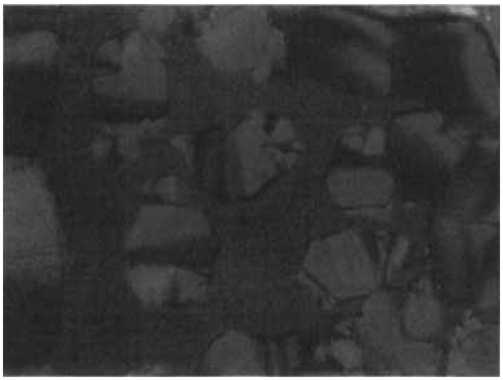


PLATE 3 Compound **4C6**, $T = 90°C$ (Toluene). (See Color Plate XIV).

Finally, the **4C12Br** complex shows the same behaviour. The melting temperature is lower than in the case of the **4C12** compound; meanwhile the clearing temperature is higher (see Tab. I). Consequently, the mesomorphic range increased from 233°C for the **4C12** complex to 271°C for the **4C12Br**.

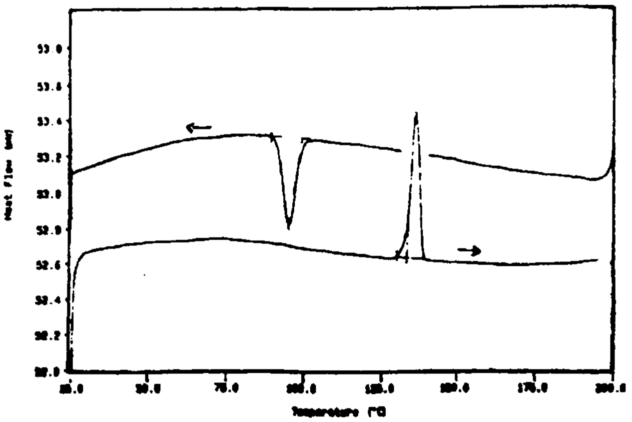
Typical DSC curves are given in Figures 1a and 1b in the case of the **4C7** and **4C4** complexes. To detect all the transitions, a **4C7** sample was first heated towards the isotropic phase. Then, to avoid any decomposition, a new **4C7** complex sample was heated only to 200°C. In such conditions (no heating over 200°C), the transition temperatures and enthalpies were reproducible and are given in Table I. The purity of the samples was then checked after the heating and cooling cycles by thin layer chromatography. A DSC curve of the **4C4** complex is given in Figure 1b. The thermogram is reproducible, two peaks can be detected upon heating (without reaching the clearing point) and cooling. In both cases, the low temperature peak ($\theta = 239°C$) has a greater enthalpy than the high temperature one ($\theta = 267°C$) and shows a great supercooling (32°C). Moreover, the transition enthalpies are of the same order of magnitude as for the other compounds.

In Figure 2 are given the melting and clearing temperatures of the **4Cn** compounds as a function of the chain length. The clearing temperatures slowly decrease from 360.6 to 332°C by increasing the chain length (from $n = 6$ to $n = 12$). The melting temperatures rapidly decrease from 267 to 112°C for the shortest chain homologues (from $n = 4$ to $n = 8$) and remain almost constant for the highest ones (from 112°C for $n = 8$ to 99°C for $n = 12$). No even-odd effect is detected upon the melting and clearing temperatures.

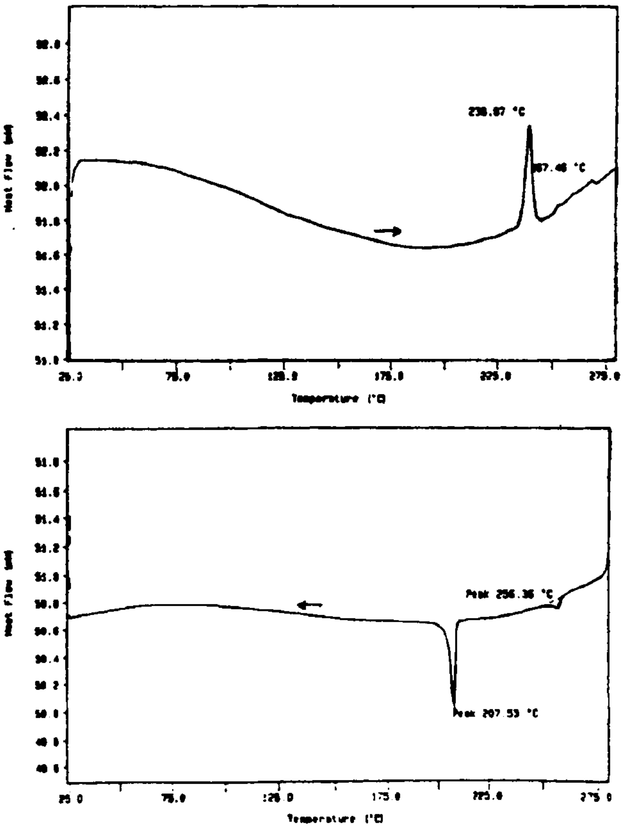
3.2. Ligand

As can be seen in Table I and as usual [1], the clearing temperature of the ligand **4C12′** is lower than the clearing temperature of the corresponding complex and no decomposition occurs. The textures presented in Plates 4 and 5 were obtained by the slow cooling of the isotropic phase of pure **4C12′** compound. On Plate 4 appear some linear defects and dendritic domains; on Plate 5, some fan-shaped textures. Such defects are characteristic of columnar hexagonal phases D_h [10, 11].

In order to take more insights into the nature of the mesophases and to have an idea of the organisation of the molecules, we have performed X-Ray studies on the complexes and the ligand synthesised. The results are summarised below.



(a)



(b)

FIGURE 1 DSC curves of **a**/ the **4C7** complex, **b**/ the **4C4** complex.

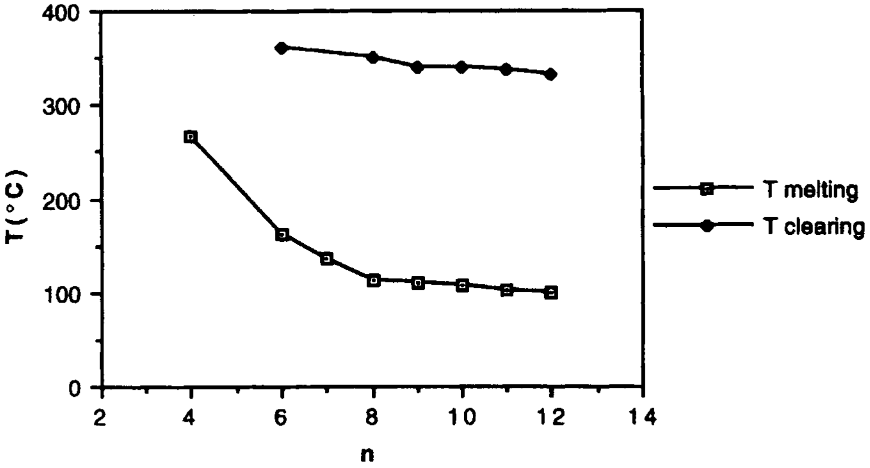


FIGURE 2 Melting and clearing temperatures of the **4Cn** complexes as a function of the chain length.

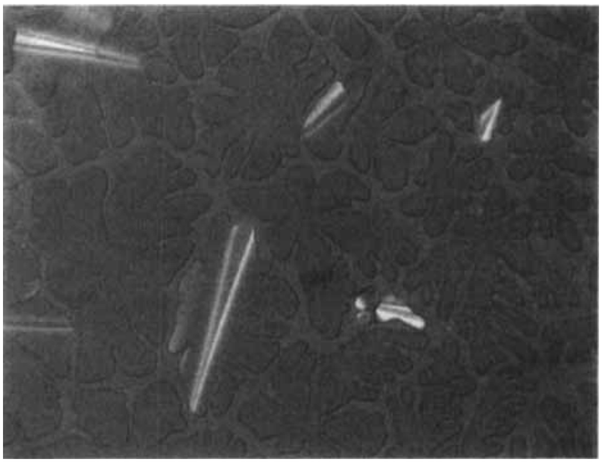


PLATE 4 Compound **4C12'**, $T = 205°C$. (See Color Plate XV).

4. X-RAYS DIFFRACTION STUDIES

Aligned samples of complexes were obtained by spreading a small amount of product onto a thin mica single crystal sheet with a spatula and patterns were taken with a set up already described [12]. A Guinier powder camera was used to measure accurately the structural parameters of the mesophase

PLATE 5 Compound **4C12'**, $T = 205°C$. (See Color Plate XVI).

of all the compounds (except for the **4C4** complex, the temperature of the mesophase being too high to be reached).

4.1. Complexes

Powder and aligned sample patterns are presented in Figures 3a and 3b for the **4C12** and **4C8** complexes respectively. On the aligned sample pattern (**4C8** complex), at small angles and on the equator, sharp lines can be detected in a spacing ratio 1, $\sqrt{3}, 2, \sqrt{7}, 3$. This is the sign of an hexagonal lattice. At wide angles and on the meridian, one diffuse crescent at $s \approx 1/3.42$ Å^{-1} can be detected which is due to the existence of some core to core interactions parallel to the column axis. Moreover, at $s \approx 1/4.9$ Å^{-1}, four diffuse spots corresponding to the molten paraffinic chains can be seen. The presence of these diffuse spots is due to some orientation of the paraffinic chains, out of the plane of the hexagonal lattice and off the column axis. No sign of any helicity can be detected on the pattern. Such a behaviour is characteristic of a columnar hexagonal phase, with $\mathbf{a} = 23.7 \pm 0.1$ Å and $\mathbf{c} = 3.42 \pm 0.01$ Å as parameters.

On the powder pattern of compound **4C12**, are detected, at small angles, Bragg peaks in ratio $1, \sqrt{3}$, 2, $\sqrt{7}$, 3, $\sqrt{13}$ (hexagonal lattice). At wide angles, two diffuse peaks appear at $s \approx 1/4.9$ Å^{-1} and $s = 1/3.42$ Å^{-1} (molten parts of the molecule). Such a pattern is once more characteristic of a columnar hexagonal phase with $\mathbf{a} = 27.1 \pm 0.1$ Å, $\mathbf{c} = 3.42 \pm 0.01$ Å. A proposed indexation of this pattern is given in Table II.

For every compounds, aligned and powder samples patterns were recorded. They all exhibit columnar hexagonal phases as suggested by the

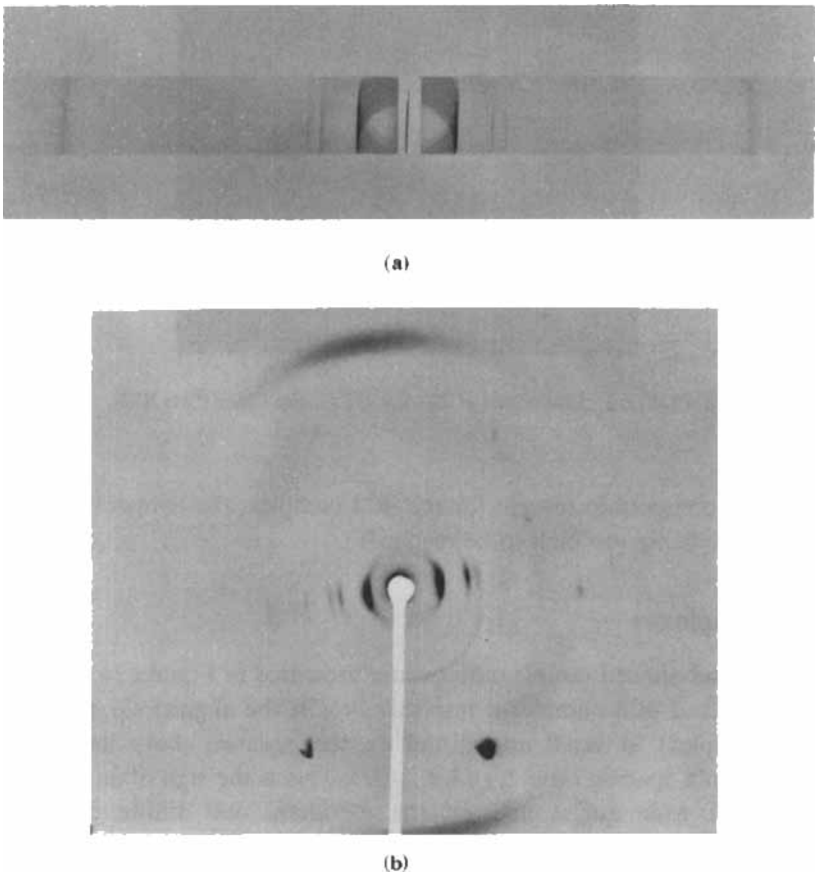


FIGURE 3 **a**/Powder pattern of the **4C12** complex, **b**/Aligned pattern of the **4C8** complex.

TABLE II Proposed indexation for the powder pattern obtained in the mesophase, upon heating compound **4C12**

hkl	*ratio*	*d(measured)Å*	*d(calculated)Å*
010 100	1	23.47	23.53
110	$\sqrt{3}$	13.55	13.58
200 020	2	11.76	11.76
210 120	$\sqrt{7}$	8.88	8.89
300 030	$\sqrt{9}$	7.92	7.84
220	$2\sqrt{3}$	–	
310 130	$\sqrt{13}$	6.50	6.53

microscopic observations. The structural parameters of the D_h phases are presented in Table III. The Figure 4 presents the variations of the parameters of the hexagonal lattice as a function of the chain length. The hexagonal lattice parameter **a** increases regularly, as expected, when increasing the chain length. On the other hand, the **c** parameter remains almost constant, between 3.36 and 3.45 Å. The smallest value is obtained with the **4C12Br** complex and the higher for the **4C12′** ligand. In any cases, such values are among the shortest encountered in columnar hexagonal

TABLE III Hexagonal lattice parameters and calculated densities of the dibenzotetraaza[14]annulene complexes and ligand

Compounds	**a** (Å)	**c** (Å)	ρ
4C6	21.9	3.42	1.05
4C7	22.7	3.40	1.04
4C8	23.7	3.42	1.00
4C9	24.4	3.39	1.02
4C10	25.5	3.38	0.98
4C11	26.0	3.40	0.98
4C12	27.2	3.42	0.94
4C12Br	27.2	3.36	1.07
4C12′	27.3	3.45	0.88

$\rho = nM/NV$ with ρ molecular density,
N Avogadro's number,
V cell volume, $V = (\sqrt{3}/2)a^2c$,
M molecular mass.

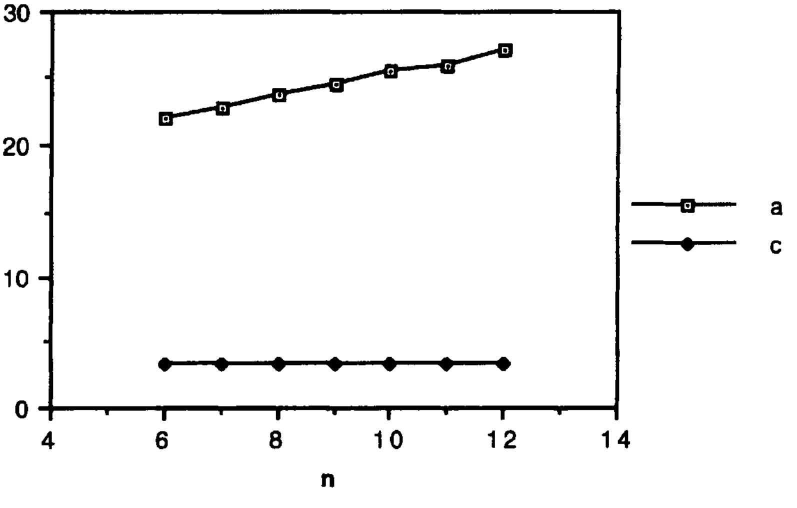


FIGURE 4 Variations of the parameters **a** and **c** with the chain length (in Å).

phases (for example, in hexaalkoxytriphenylenes, $c = 3.6$ Å [13]). They can be compared with the **c** values observed in the case of some pyrylium salts and are certainly due to the existence of strong π–π interactions between the molecules [1].

The number of molecules per unit cell can be calculated according to:

$\rho = n\,M/NV$ where n is the number of molecules per unit cell; ρ, the molecular density; N, the Avogadro number; V, the unit cell volume, $V = (\sqrt{3}/2)\mathbf{a}^2\mathbf{c}$ and M, the molecular mass. Moreover, assuming that the density in a mesophase is closed to one, $n = 1.07$ for the **4C12** compound. So, the number of molecules per unit cell is one and then, if $n = 1$, the calculated density is 0.94. Table III shows also the calculated densities from the **4C6** to **4C12** and **4C12Br** complexes as for the ligand **4C12′**, which all have one molecule per unit cell. As can be seen, the density slowly decreases by increasing the chain length, except in the case of the **4C12Br** which exhibits the highest density, due to the presence of the bromine atoms. The smallest value is found in the case of the free macrocycle and is due to the absence of any atoms with high electronic density.

From the aligned patterns, it is also possible to calculate the intracolumnar correlation length L_p, corresponding to the length of columns where exist some core to core interactions. This was done in the case of the **4C8**, **4C10** and **4C12** complexes and is given in Table IV. Such a distance slightly increases from 147 Å ($n = 8$) to 167 Å (for $n = 12$) which means that, in the correlation length, 45 to 50 molecules are found regularly stacked.

The volume of each hexagonal cell was also estimated ($V = \sqrt{3}/2)\mathbf{a}^2\mathbf{c}$) and drawn as a function of the total number of the carbon atoms grafted on the macrocyclic core. This is presented in Figure 5. The slope of this curve gives the mean volume per added methylene group $V_{\mathrm{CH2}} = 30$ Å^3, which is an usual value in the case of D_h phases [1]. The intersection of the curve with the y axis gives the apparent volume of the core $V_{\mathrm{core}} = 680$ Å^3, which leads to an apparent radius $R_{\mathrm{core}} = 7.98$ Å. A model with an optimised geometry (Hyper Chem modelling software) is given in Figure 6. It shows that the molecule is saddle shaped *ie* non planar and moreover, non strictly discotic. The two characteristic dimensions are 14.4 and 10.7 Å. So, the

TABLE IV Correlation length and corresponding number of molecules of complexes **4C8**, **4C10** and **4C12**

	4C8	4C10	4C12
Lp (Å)	147	145	167
Corresponding number of molecules	45	44	50

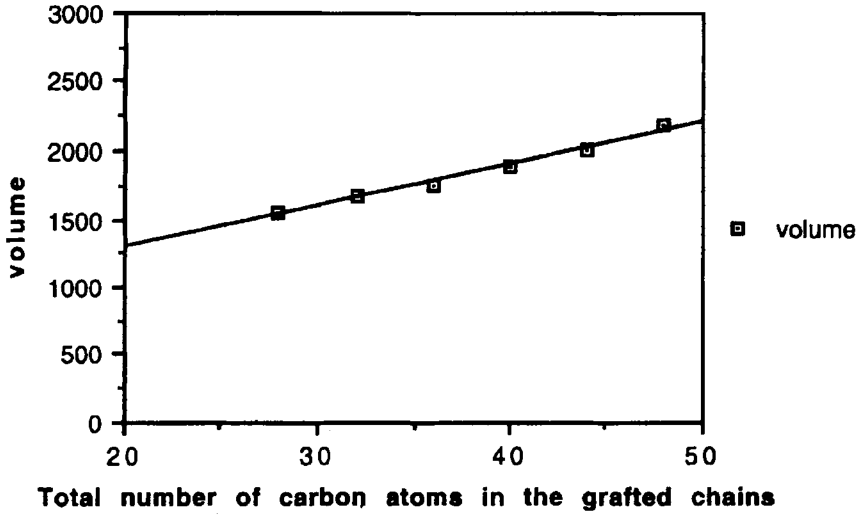


FIGURE 5 Volume of the unit cells as a function of the total number of carbon atoms in the **4Cn** complexes.

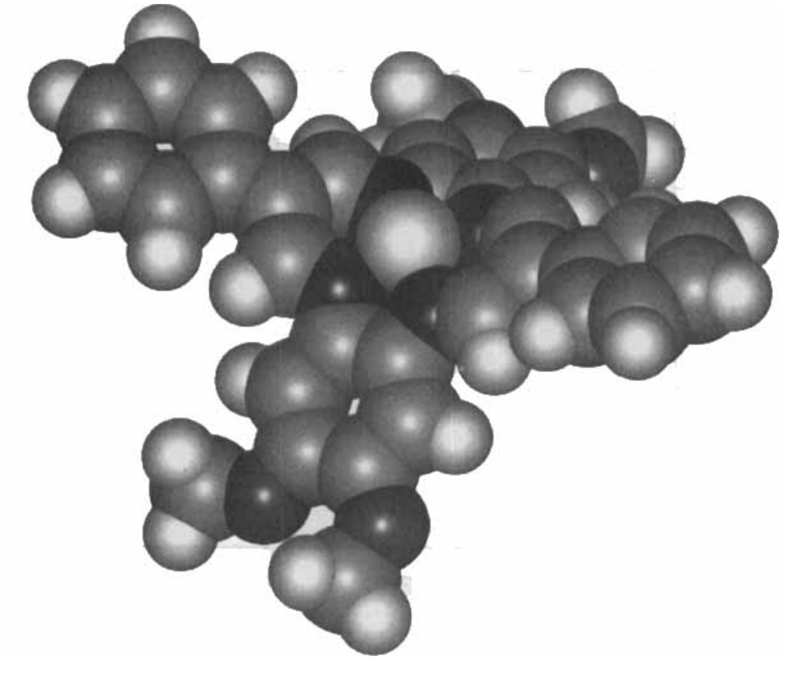


FIGURE 6 Molecular model with an optimised geometry (Hyper Chem software).

apparent radius can be compared to half of the longer dimension (7.2 Å). With the apparent value R_{core}, it is possible to calculate the apparent length of the aliphatic chains (l) and to compare it with the length of a paraffinic chain in an all trans conformation (L). The ratio L/l will give an idea upon the bending of the chains in the studied complexes. Figure 7 gives this ratio as a function of the chain length. It is quite constant and comprised between 2.32 and 2.59. This means that the chains are very mobile, even if slightly oriented, and in a highly molten state. This is not surprising since they have to fill all the space around the macrocycle, especially the area corresponding to the non-substituted phenyls.

In conclusion, we have shown that dibenzotetraaza[14]annulene complexes, substituted by four paraffinic chains exhibit, despite the geometry of the macrocycle, columnar hexagonal phases, D_h. The clearing temperatures are very high (up to 300°C) and the mesomorphic range is wide for the higher homologues. As usual, the corresponding ligand has a lower transition temperature. It also shows a columnar hexagonal phase. When adding bromine atoms on the macrocycle, the mesomorphic range increases.

The volume per methylene group, the apparent volume of the unit cells, the number of molecules per cells were determined. The presence of core to

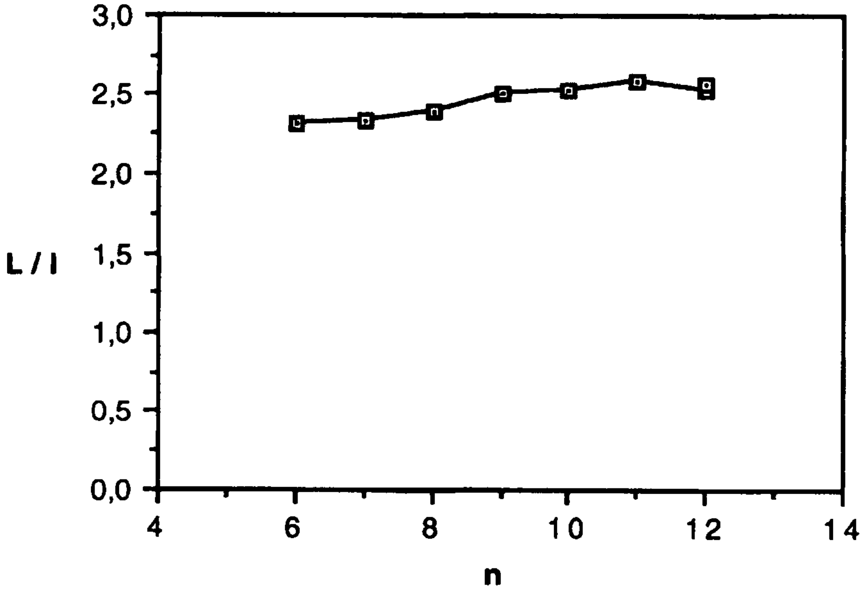


FIGURE 7 Bending state (L/l ratio) of the chains in the 4Cn complexes as a function of the chain length.

core interactions, the correlation length of the columns as well as the small value of the parameter **c** (one of the smallest for D_h phases) suggest that there are strong $\pi-\pi$ interactions within the columns. The smallest **c** value is for the dibenzotetraaza[14]annulene complex substituted by two bromine atoms. Finally, the high molten state of the chains, (and certainly some motions of the phenyls in the positions 6 and 13 of the macrocycle) explains the observation of the D_h phases for all the compounds studied: the complexes and the ligands.

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