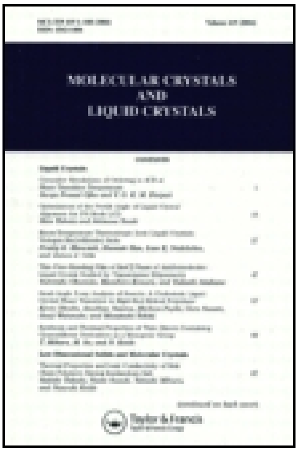

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Further X-Ray Studies of Mesophase Structure of Hexakis(Alkylsulfono)Benzene (HASBn) and Tribenzocyclononene (ll-n) Homologues

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Further X-Ray Studies of Mesophase Structure of Hexakis(Alkylsulfono)Benzene (HASBn) and Tribenzocyclononene (II-n) Homologues

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Mesophase forming compounds of hexakis(alkylsulfono)benzene compounds (HASBn) are found for $n = 7$ to 15 carbons per sidechain. We compare X-ray studies for $n = 14$ with previous results for $n = 13$. The diffraction patterns indicate a more disordered structure for $n = 14$, even in the room temperature crystalline phase. The mesophase diffraction pattern is consistent with hexagonal packing of disordered discotic columns, with average lattice repeat $a = 29.3$ Å. The (10), (11), and (20) reflections are observed with the last one being barely detectible. A fourth broad scattering peak centered about a spacing of about 5.0 Å is attributed to the spacing between molecules within the columns. These numbers are slightly larger than the corresponding numbers for $n = 13$, as should be expected.

Four different homologous series of tribenzocyclononene compounds have been studied. Compounds in series II having 8 to 15 carbon atoms per sidechain exhibit mesomorphism, with structures based on columns of pyramidic or "bowlic" molecules. We compare results obtained from compound II–15 (15 carbon atoms per sidechain) with results obtained from other compounds in this series. The diffraction pattern indicates considerably more disorder for II–15 than for II–13 at all temperatures.

Out of five observed features in the hexagonal mesophase, 4 diffraction lines are most simply indexed in terms of a lattice parameter of 59.7 Å. The (11), (20), (22) and (40) reflections are observed but not the (10) reflection.

Keywords: structure of mesophase, x-ray diffraction

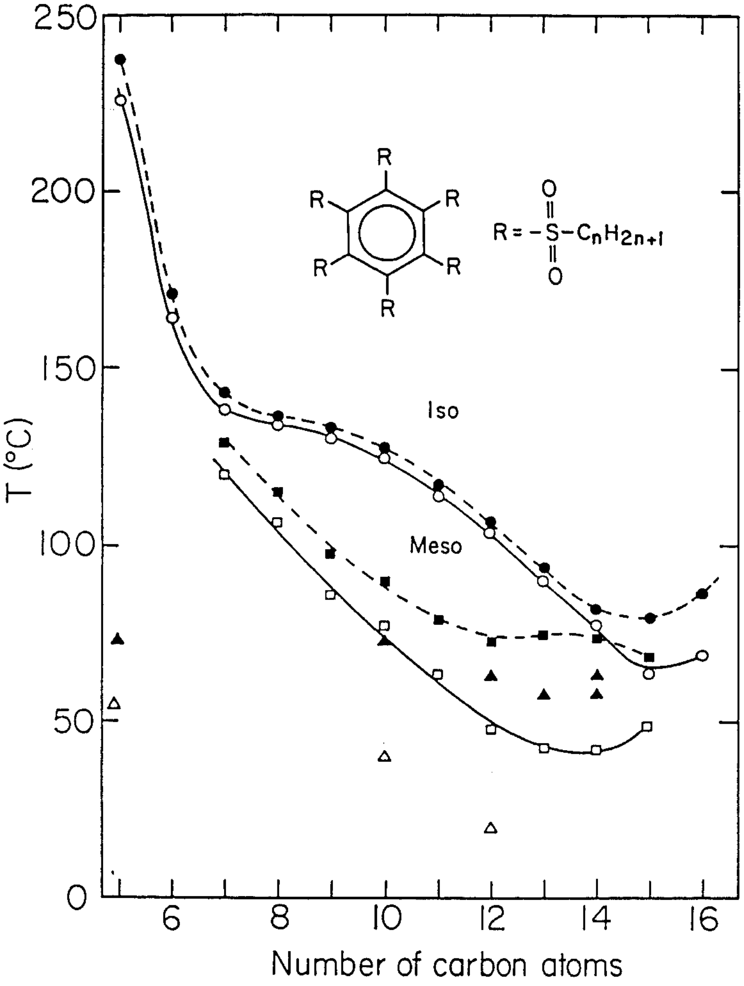

FIGURE 1 Transition temperatures in the hexakis(alkylsulfono)benzene series for $5 \leq n \leq 16$, based on DSC measurements.[5] Open symbols are for transitions with decreasing temperature; solid symbols for increasing temperature. Circles are for isotropic-mesophase, squares for mesophase-solid, and triangles for solid-solid transitions.

INTRODUCTION

We report X-ray measurements on the solid and mesomorphic phases of the discotic liquid crystal HASB14, a homologue of the hexakis(alkylsulfono)benzene series (HASBn),[1-5] and the pyramidic liquid crystal II–15, a homologue of the hexaalkanoyloxytribenzo-cyclononene series (II–*n*).[6-13] The results provide information on the structure of the mesophases, in particular the intra- and intermolecular spacings and the overall symmetry of the mesophases. X-ray measurements have been previously reported on HASB13[16] and three members of series II–*n*, *n* = 10, 12[9] and *n* = 13.[14] These studies agree with the columnar structures and sym-

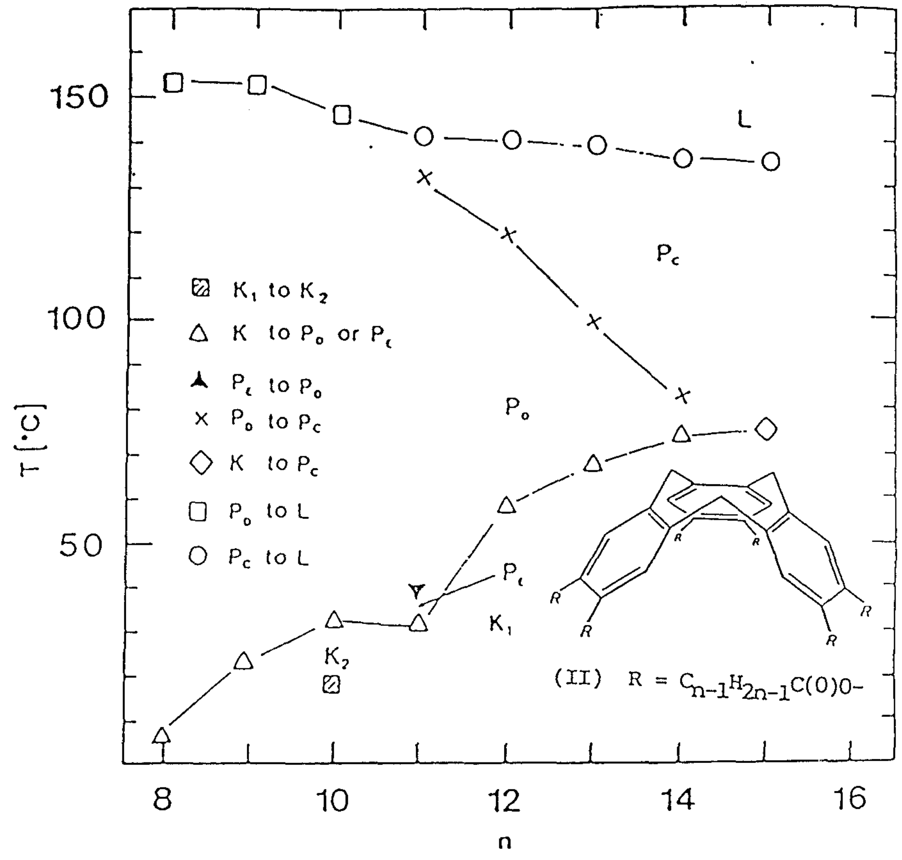

FIGURE 2 Schematic representation of the phase transition temperatures for the hexaalkanoyloxytribenzocyclononene (II–*n*) homologues.

metries of mesophases as determined by optical microscopy observations. Phase diagrams for these two systems are shown in Figures 1 and 2. The molecular geometries are also shown in the figures.

X-RAY MEASUREMENTS

The powder X-ray measurements on the HASB14 and II–15 homologues were made using a modified vertical scanning Philips diffractometer with transmission specimen and focussing LiF (200) monochromator adjusted for CuK_α radiation (weighted wavelength 1.5418 Å) in the incident beam, and a temperature controlled specimen stage similar to one previously described.[15] The present instrument operates under computer control. Samples of HASB14 and II–15 for the powder diffraction measurements were hermetically sealed in disc-shaped specimens which were 0.5 mm thick and covered at top and bottom with 25 micron aluminum foil.

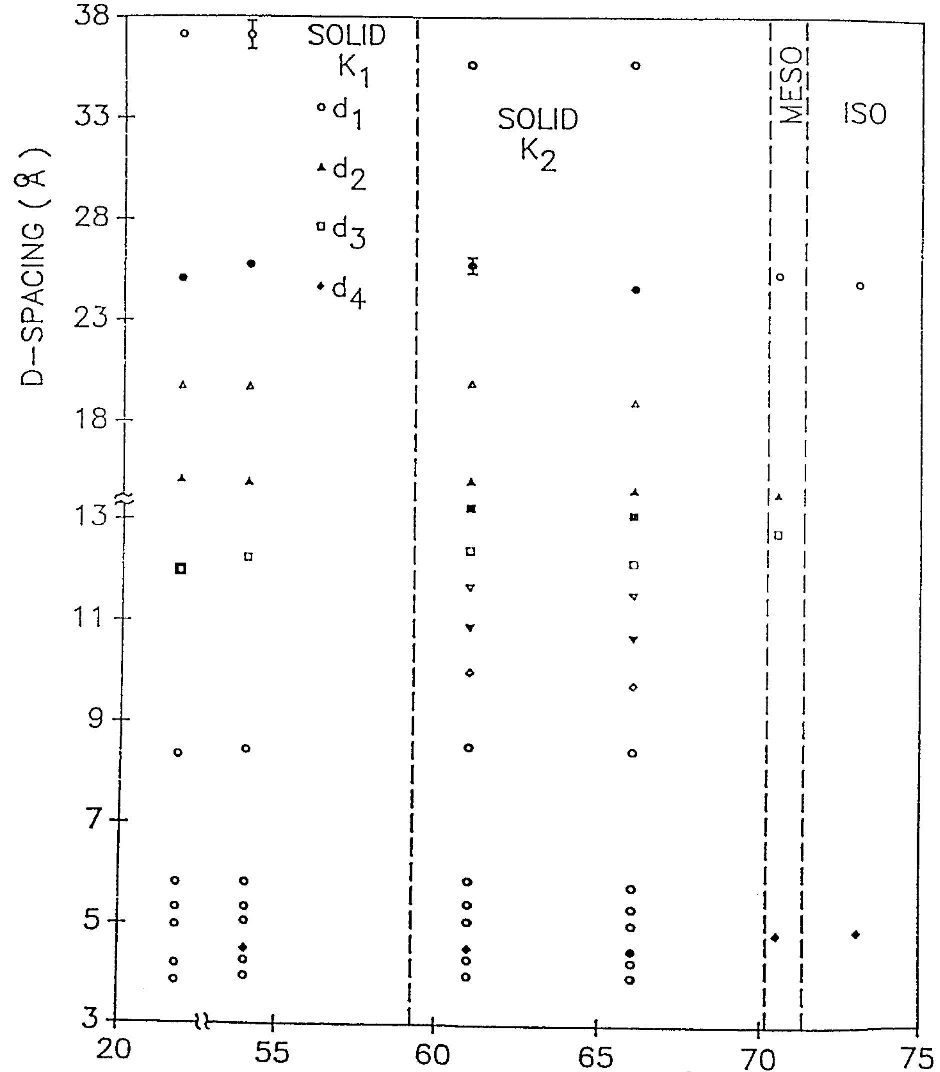

FIGURE 3 *d*-spacings as a function of temperature for x-ray powder diffraction lines of HASB14.

To minimize the temperature gradients in the sample, for some of the measurements the specimen chamber was covered with additional sheets of aluminized mylar (total thickness 21 microns) while the sample holder itself was modified to be heated from both above and below. (The aluminized mylar sheets were mounted well off the parafocusing circle, so that their effect on the observed diffraction patterns was negligible.) The X-ray tube was operated at 640W (32 kV, 20 mA) for all these measurements. It was necessary to make repeated scans over some parts of the diffraction pattern to assure sufficient statistical precision in the measurements.[14]

TABLE I

Widths and intensities of HASB14 diffraction lines

K_1 (54°C)			K_2 (61°C)			Meso (70.5°C)		
d(Å)	$W_{1/2}$ (deg2Θ)	I_{peak}	d(Å)	$W_{1/2}$ (deg2Θ)	I_{peak}	d(Å)	$W_{1/2}$ (deg2Θ)	I_{peak}
37.11	0.55	12910	35.62	0.36	13250			
25.76	0.92	3963	25.76	0.45	5494	25.39	1.65	1500
19.72	0.78	2595	19.95	0.34	3710			
15.03	0.57	1237	15.16	0.35	1859	14.65	0.77	486
			13.85	0.50	911			
12.23	0.80	1399	12.40	0.45	1412	12.76	0.85	405
			11.66	0.47	931			
			10.88	0.44	961			
			9.96	0.41	645			
8.44	1.13	366	8.52	0.90	427			
5.82	1.40	588	5.86	1.16	669			
5.33	1.48	660	5.40	1.20	807			
5.05	1.51	879	5.05	1.29	1017			
4.50	1.05	2260	4.52	0.71	2329	4.83	2.14	700
4.27	1.73	1610	4.30	0.95	1762			
3.96	1.20	856	3.97	1.00	941			

COMPOUND HASB14

Because the mesomorphic phase for HASB14 is only about 1°C wide, it was found necessary to modify the temperature stage as described above to reduce the temperature gradients within the sample. Without this modification it was not possible to make measurements with the entire sample in the mesomorphic phase. Also because of the narrow temperature range of the mesophase, measurements were possible at only one temperature. Four different diffraction maxima were observed, three of which we assign to packing of columns in a two-dimensional net and the fourth to the average stacking distance between the molecules within a column.

TABLE II

Experimental and calculated *d*-spacings for the mesophase of HASB14 indexed on a two-dimensional hexagonal net with $a = d_1/\text{Sin}60 = 29.32$ Å at 70.5°C

d(hk)	d(meas)Å	d(calc)Å	Deviations(Å)
$d_1(10)$	25.39	------	------
$d_2(11)$	14.65	$\sqrt{3}d_2 = 25.37$	$d_1-\sqrt{3}d_2 = 0.02$
$d_3(20)$	12.76	$2d_3 = 25.52$	$d_1-2d_3 = -0.13$
d_4	4.80	------	------

COMPOUND II-15

For compound II-15, measurements were made at seven different temperatures within the mesophase region, as well as in the solid and isotropic phases. Five different features were observed in the mesophase, four of which we assign to the packing of columns and the fifth to the intracolumnar stacking distance (Table III). Of the first four peaks one was very weak (2 counts/sec above a background of 11 counts/sec), but was well established.

RESULTS AND DISCUSSION

The discussion is divided into two parts corresponding to the results obtained from the two different systems.

COMPOUND HASB14

The solid phases: Before discussing the diffraction data of the mesophase we briefly comment on the results obtained from the solid phases. Just as was found for HASB13,[16] there seems to be a second solid state phase, with transition temperature in the vicinity of 58°C. This can be seen from Figure 3 which shows the observed *d*-spacings as a function of temperature. Twelve lines were observed in phase K_1 (lower temperature phase) and 16 lines in phase K_2 were observed. Moreover, the diffraction lines are narrower in K_2 than in K_1. Peak intensities and widths at half peak intensity are tabulated in Table I. Because we observed only 12 or 16 powder diffraction lines, it is not possible to draw definitive conclusions regarding the structures of these phases, other than that they are not cubic or hexagonal.

The mesophase: On increasing the temperature of HASB14 from room temperature a marked change in the diffraction pattern was observed at just above 70°C, signalling the solid-mesophase transition. The number of diffraction peaks decreased from 16 to 4. The *d*-values for the mesophase peaks, measured at 70.5°C are given in Table II. Of the four peaks in the mesophase, two, namely d_2 and d_3,

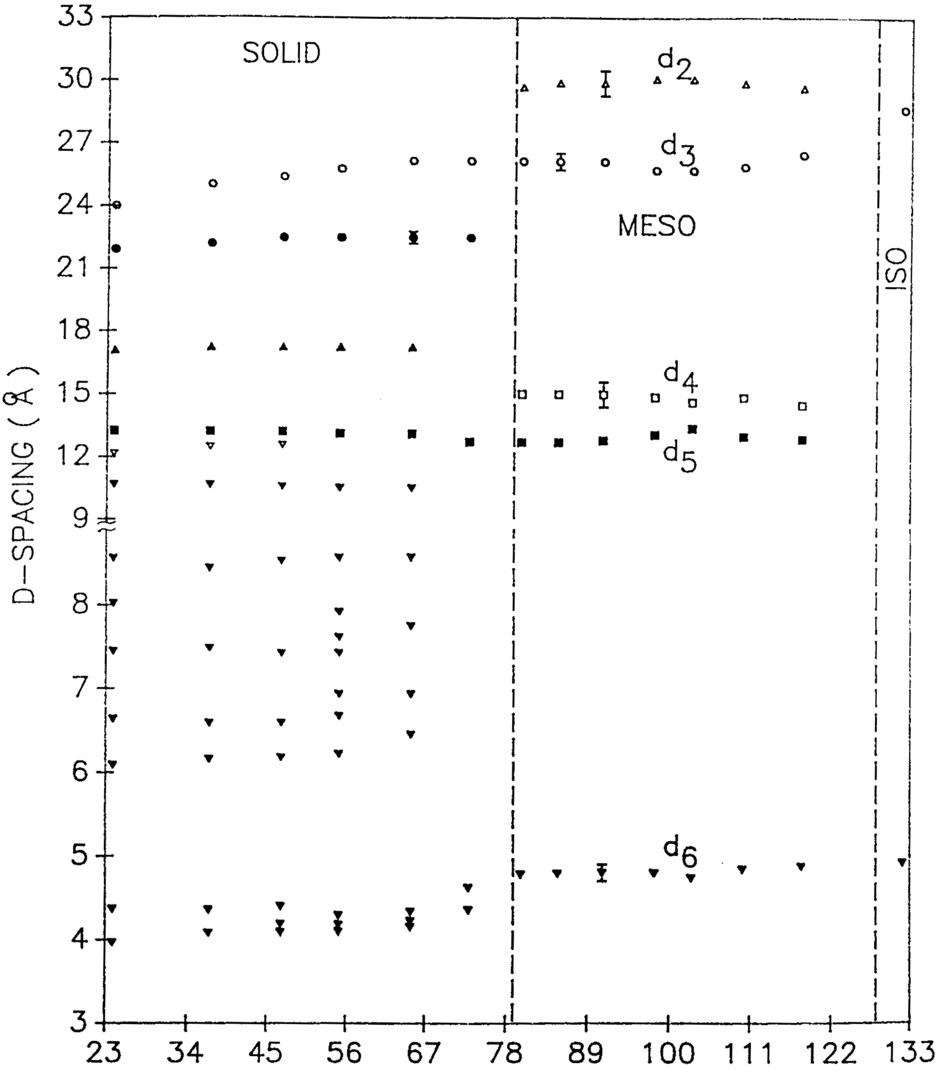

FIGURE 4 *d*-spacings as a function of temperature for x-ray powder diffraction lines of II–15.

were very low in relative intensity. At the isotropic transition temperature (about 71°C) these two lines became undetectable and the width of the remaining two peaks increased considerably while their peak intensities decreased. The line width is also shown in Table I. The spacings corresponding to the d_1, d_2 and d_3 peaks in Figure 3 are in the ratio $1{:}1/\sqrt{3}{:}\frac{1}{2}$, as shown in Table II, suggesting a hexagonal symmetry, similar to the results for HASB13 obtained by Spielberg *et al.*[16]

The lattice parameter of a = 29.32 Å for HASB14 may be compared with a = 25.70 Å for HASB13. The larger value for HASB14 is expected because of the additional carbon atom per side chain. As with other discotics we identify this

TABLE III

Experimental and calculated *d*-spacings for the P_c mesophase of II–15 indexed on a two-dimensional hexagonal net with $a = d_1/\text{Sin}60 = (29.85\ \text{Å})(\sqrt{3})/\text{Sin}60 = 59.7\ \text{Å}$

Miller Indices hk	d(meas)Å*	d(calc)Å
10	-------	51.70 (d_1)
11	29.85 (0.15)	29.85 ($d_2 = d_1/\sqrt{3}$)
20	26.06 (0.25)	25.85 ($d_3 = d_1/2$)
22	14.87 (0.18)	14.93 ($d_4 = d_1/\sqrt{12}$)
40	12.98 (0.22)	12.93 ($d_5 = d_1/4$)
**	4.8(0.03)	(d_6)

* Average values over the mesophase region (numbers in parentheses are rms deviations from the average values).

** This value corresponds to the intracolumnar stacking distance of the molecules.

parameter with the average distance between the columns in an hexagonal array. The fourth scattering peak at 4.8 Å, is not significantly different from the value found for HASB13 (4.9 Å) and is ascribed to the average stacking distance of the molecules within the columns. In the solid phase, for HASB13,[16] the largest *d*-spacing was reported as 35 Å and for HASB14 we obtained 37 Å. As with the HASB13 data we consider that the HASB14 molecules in the solid phase are also in the all-trans conformation. On going to the mesophase there is a sharp reduction in the largest *d*-spacing, i.e., from 37 Å to 25.39 Å, indicating that in the mesophase the side chains are considerably disordered. From Table I, it is seen that the mesophase line d_4 is considerably broader than any solid phase lines and the other mesophase lines, confirming the disordered nature of the columnar stacking. We therefore identify the mesophase as D_{hd} columnar discotic with one molecule per unit cell.

COMPOUND II–15

As expected from the phase diagram (Figure 2) only the P_c uniaxial mesophase is observed, with a transition from the solid at 80°C. Previous X-ray studies of the P_c mesophase were carried out by Levelut *et al.*[9] using the homologue II–12 and by Poupko *et al.*[14] for the homologue II–13, both of which, unlike II–15, exhibit P_d and P_c instead of only the P_c phase. The results for the P_c mesophase of II–12 and II–13 were interpreted in terms of a 2D-hexagonal phase with 4 molecules per unit cell.

Five features were observed in the mesophase diffraction pattern. As shown in Figure 4, the *d*-spacings for these features were essentially independent of tem-

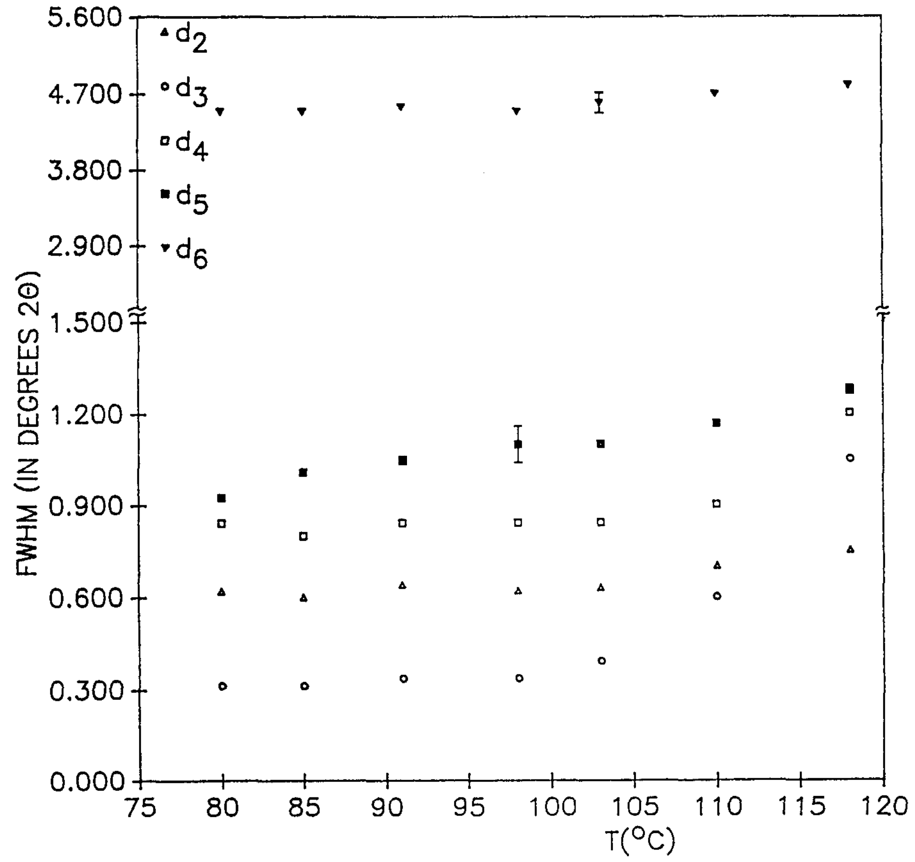

FIGURE 5 Width at half-maximum intensity, FWHM, of x-ray diffraction peaks in the mesophase of II–15.

perature within the mesophase region. Four of the features can be indexed on the basis of a 2D-hexagonal lattice (Table III) with a lattice parameter of a = 59.7 Å. Since the specific gravity of the mesomorphic phases is close to unity, we conclude that there are four columns per unit cell just as for II–12[9] and II–13.[14] We note that reflections having Miller indices (11), (20), (22), and (40) were detected but the reflection (10) was not detected, either because it is absent or because of the extremely high background intensity in the low angle region. The lattice parameters of II–12 and II–13, reported as 49.38 Å and 52.77 Å respectively, are consistent with that of II–15, namely 59.7 Å.

In the P_c mesophase for sample II–15 the line width of d_6 (note that the missing (10) reflection is designated as d_1) increases slowly with temperature as shown in Figure 5, indicating an increase in disorder of the stacking as the clearing point is approached. The widths of the other mesophase lines increase more rapidly with temperature, indicating an increase in the disorder of packing of the columns. On passing the clearing point, only two very broad lines, with peaks presumably corresponding to the diameter and thickness of the molecule, are observed. The

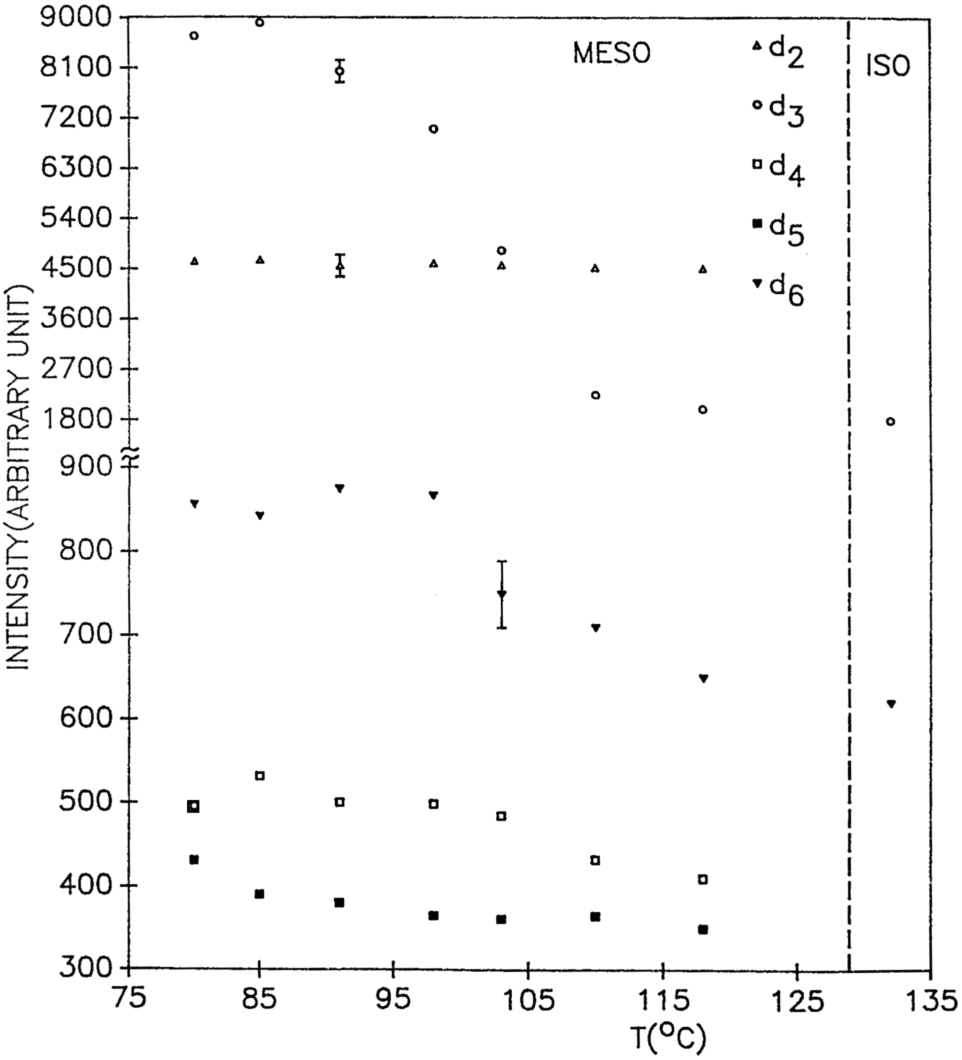

FIGURE 6 Peak intensities of the diffraction lines in the meso- and isotropic phases of II-15 as a function of temperature.

intensities of the various reflections in the mesophase remain relatively constant except for d_3 (26.06 Å), which decreases rather markedly, as shown in Figure 6.

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