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FLUORINATED ANALOGUES OF LIQUID CRYSTALS II. STRUCTURE OF THE SMECTIC PHASE OF 1,6-DI(*p*-TOLYL)-PERFLUOROHEXA-1,3,5-TRIENE

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Abstract: The smectic phase of 1,6-di(*p*-tolyl)-perfluorohexa-1,3,5-triene has been studied using X-ray diffraction and optical modelling. A "translational" type of packing with a shift of the molecules by half of their length is proposed. This arrangement of molecules agrees with the single crystal diffractometry data.

It has been reported recently[1] that member compounds of the α,ω-diarylperfluoropolyene series

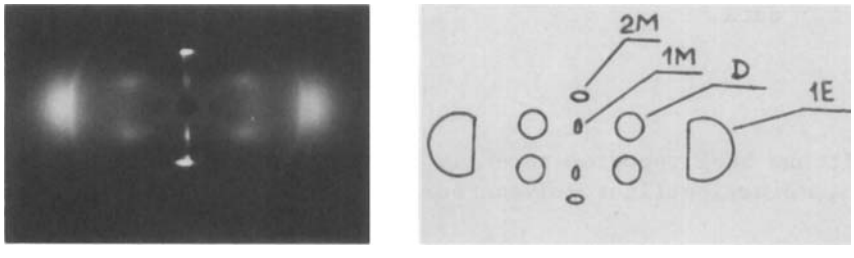
$$p\text{-R-C}_6\text{H}_4\text{-(CF = CF)}_n\text{-C}_6\text{H}_4\text{-R-}p$$

with R = CH_3, OCH_3; n = 2, 3, 4, possess the properties of liquid crystals. 1,6-Di(*p*-tolyl)-perfluorohexa-1,3,5-triene (R = CH_3, n = 3) (I) forms smectic (Figure 1) and nematic phases as follows:

$$\text{Cryst}_1 \xleftrightarrow{85^\circ\text{C}} \text{Cryst}_2 \xleftrightarrow{120^\circ\text{C}} \text{S} \xleftrightarrow{145^\circ\text{C}} \text{N} \xleftrightarrow{176^\circ\text{C}} \text{IL}$$

To find out the structure of the smectic phase of (I) an X-ray diffraction study of oriented samples was carried out. The oriented smectic phase was obtained by cooling the nematic phase in a magnetic field of 10,000G.

Figure 1: Polygonal texture of the smectic phase of (I). Crossed polarizers, 155°C, x 200.



(a) (b)

Figure 2: (a) - X-ray photograph of the oriented smectic phase of (I), 155°C.
(b) - Scheme of specification of reflections shown in Figure 2(a).

A typical X-ray photograph is shown in Figure 2(a),(b). There are two meridional reflections of first order (1 M), two of second order (2 M), four diagonal reflections (D), and two equatorial reflections (E).

An X-ray diffraction photograph with a similar arrangement of reflections was not previously observed. The decrease in intensity of the reflections 1 M, the increase for the reflections 2 M and the appearance of diagonal reflections (D) suggest an unusual arrangement of molecules in this smectic phase.

From the diffraction pattern it is possible to calculate, using Bragg's equation, the thickness of the smectic layer and the average distance between the long axes of the neighbouring molecules.

The following interplanar distances were calculated:

Reflection	Interplanar distances
1 M	19.7 Å
2 M	19.7 Å
1 E	4.5 Å

The length of the molecule according to stereochemical data is about 19.8 Å. The value of 4.5 Å is usual for intermolecular distances in the smectic plane.

Using the extinction condition $\Delta d = d/2\ m$, where Δd is the periodic translation of molecules along their long axes, d is the thickness of the layer, and m is the order of the reflections, it can be found that extinction of the meridional reflections of the first order is caused by a translational shift of the molecules by a magnitude d/2.

To check this suggestion we used the method of optical analogy.[2]

A graphic model of the molecular arrangement with a translational shift of d/2 and orientational disordering was constructed (Figure 3).

The diminished mask was illuminated by a He-Ne laser beam. The intensity distribution on the diffraction pattern obtained (Figure 4) is in accordance with the X-ray photograph:

(1) the 1 M reflections are weak;
(2) four diagonal reflections are observed.

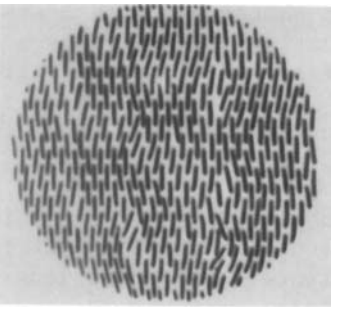


Figure 3: Graphic model of the molecular arrangement in the smectic phase of (I).

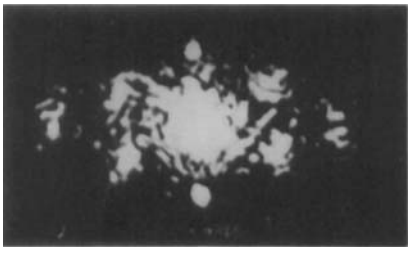


Figure 4: Optical diffraction pattern from the graphic model.

To find out the molecular and crystal structure of (I), X-ray single crystal diffractometry was carried out.

From single crystal diffractometry, Mo K_α, λ = 0.710 Å; a = 9.520 (3), b = 9.537 (2), c = 10.389 (2) Å; α = 106.48 (2), β = 94.19 (2), γ = 105.13 (2)°; z = 2, space group P 1. Independent reflections numbering 2358 were measured with an automatic four circle Syntex 2 P/1 diffractometer; 1720 of those with $F^2 > 2\sigma$ were used in the refinement.

The orientation of the phenyl rings was found from a Patterson map. Other atoms were located by Fourier-synthesis, and H atoms were found from difference Fourier-synthesis. The structure was refined by a full-matrix least squares procedure with anisotropic (isotropic for H atoms) thermal parameters, R = 0.08.

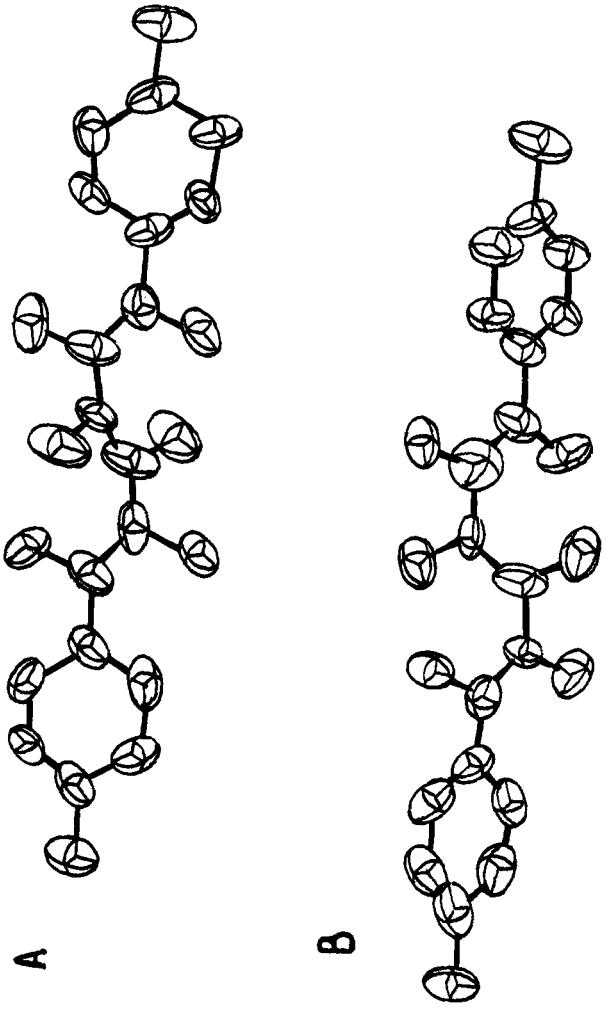


Figure 5: General view of the molecules (I).

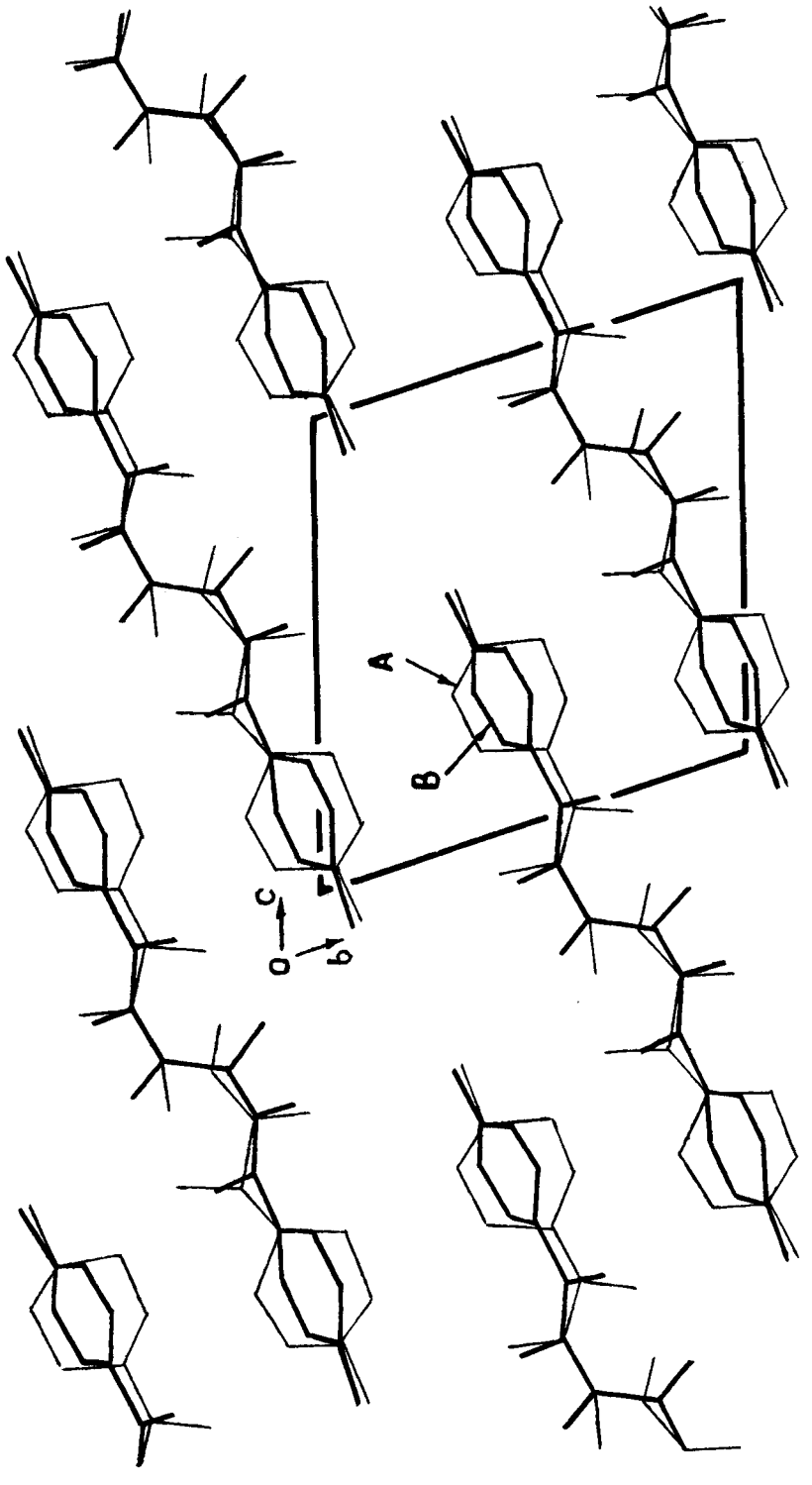


Figure 6: Packing of the molecules (I) in the crystal.

The general view of two independent molecules, A and B of compound (I), is shown in Figure 5. The symmetry of the molecules is near C_i; the planes of the phenyl rings formed a dihedral angle of 3.34° (for molecule A) and 3.21° (for molecule B). The molecules under investigation have a non-planar S-cisoid conformation, and the dihedral angle between the planes of the difluoroethylene groups is within 46.1 - 49.9°.

Figure 6 shows the packing of the molecules (I) in the bc-plane. The molecules are packed in layers along the $\vec{a}$ axis, the layers themselves being shifted in relation to each other along the long axes by d/2.

Thus, the proposed "transitional" type of molecular arrangement in the smectic phase of compound (I), is in accordance with its solid crystal structure.

References

1 VM Yurchenko, YuP Yegorov, VA Khranovski, *et al.*, *Ukr Phys J*, *23*, 337 (1978).

2 BK Wainstein, *X-ray Diffraction on Chain Molecules*, Acad Sci, USSR, Moscow, 1963.