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X-Ray Diffraction Studies of Homologous Series of 4-Alkyl-4'-Cyanostilbene

SARAMA BHATTACHARJEE and LEONID V. AZÁROFF

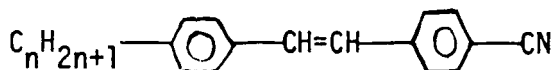
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Various members of the series 4-alkyl-4'-cyanostilbene ($n=4, \dots, 11$) have been examined by x-ray diffraction using monodomain samples aligned in .2 T magnetic field. A moving-film technique has been employed with Fe K α radiation ($\lambda=1.937 \text{ \AA}$) to record the zero level and upper levels in reciprocal space. Lower members ($n=4,5,6$) form only a nematic phase; higher members ($n=10,11$) form only a smectic-A phase; while intermediate members ($n=7,8,9$) form both nematic and smectic-A phases. The equatorial reflections were used to establish effective side-chain separations while meridional reflections permitted the calculation of effective molecular lengths and layer thickness, respectively, in the nematic and smectic phases. These were found to be longer than the calculated molecular length in its most extended conformation. For the smectic-A phases, this implies some type of bilayer structure like that reported for other liquid-crystal compounds having polar end groups.

Keywords: 4-alkyl-4'-cyanostilbene, x-ray diffraction, smectic, nematic, moving-film technique, partial bilayer

INTRODUCTION

It has been known for some time that certain cyano derivatives form smectic-A phases in which the layer spacing d , as measured by x-ray or neutron diffraction, is considerably larger than the molecular length.^{1,2} In order to investigate whether other cyano compounds show the same behavior, an x-ray diffraction study was undertaken using compounds in the series 4-alkyl-4'-cyanostilbene:



where n ranges from $n=4$ to $n=11$.

EXPERIMENTAL PROCEDURE

The compounds of the homologous series of 4-alkyl-4'-cyanostilbene (alkyl chain length $n = 9$ to 11) had been synthesized by Cox *et al.*³ and were used without further purification.

The x-ray measurements were performed using a Buerger precession camera equipped with a magnet ($H = .2$ T) and heating arrangement.⁴ The samples were placed in Lindemann-glass capillaries having square (1 mm^2) cross sections oriented at right angles to the magnetic field lines and the incident x-ray beam (at the zero camera setting). The temperature of the sample was maintained within $\pm 2^\circ\text{C}$ as determined by a thermocouple placed adjacent to the sample. Mn-filtered Fe radiation ($\lambda = 1.937\text{ \AA}$) was used to obtain optimal dispersion of the diffraction maxima which were recorded on a flat film using Laue as well as precession geometry. The centers of the diffraction maxima were determined by a film reader (as well as by locating their maximum optical densities with a Quantimet image analyzer).

RESULTS AND DISCUSSION

The transition temperatures of 4-alkyl-4'-cyanostilbenes are listed in Table 1. X-ray diffraction (Laue) photographs typical of magnetically aligned nematic and smectic-A phases are reproduced in Figure 1. The smectic layer spacings d and the intermolecular distances along the director in the nematic phase were calculated from the inner reflections along the meridian using the Bragg equation. These measured d values are listed in Table 2 as are the side-to-side spacings D ($= 1.155 \lambda/2 \sin \theta$) calculated by assuming short-range order (hexagonal) packing.⁵ For comparison purposes, Table 2 also lists the molecular length L calculated in its most extended conformation, projected on the axis of minimum moment of inertia, using standard bond lengths, angles, and Van-der-Waal's radii.

Several features are noteworthy. The interlayer spacings d for the smectic-A phases having $n = 9, 10$, and 11 are about 50% longer than the calculated molecular lengths L . (Column headed d/L in Table 2.) This has been observed previously⁶ for compounds having polar end groups and can be explained by assuming a bilayer molecular array. It is noteworthy that d/L declines slightly but progressively as the molecular length (n) shortens, suggesting a lessening in the parallelism of adjacent molecules. A corresponding increase in the average side-

TABLE I

Transition temperatures³ between crystal (*C*), smectic-A (*S_A*), nematic (*N*), and isotropic liquid (*I*) phases. (In deg. *C* with a dash indicating absence and a dot presence of phase.)

<i>n</i>	<i>C</i>	<i>S_A</i>	<i>N</i>	<i>I</i>
4	.	70.5	—	82.3 .
5	.	55.1	—	101.0 .
6	.	51.2	—	86.1 .
7	.	59.5	.. 64.6	95.0 .
8	.	51.1	. 78.7	89.4 .
9	.	56.2	. 94.4	96.7 .
10	.	47.2	. 95.1	—
11	.	65.5	. 100.2	—

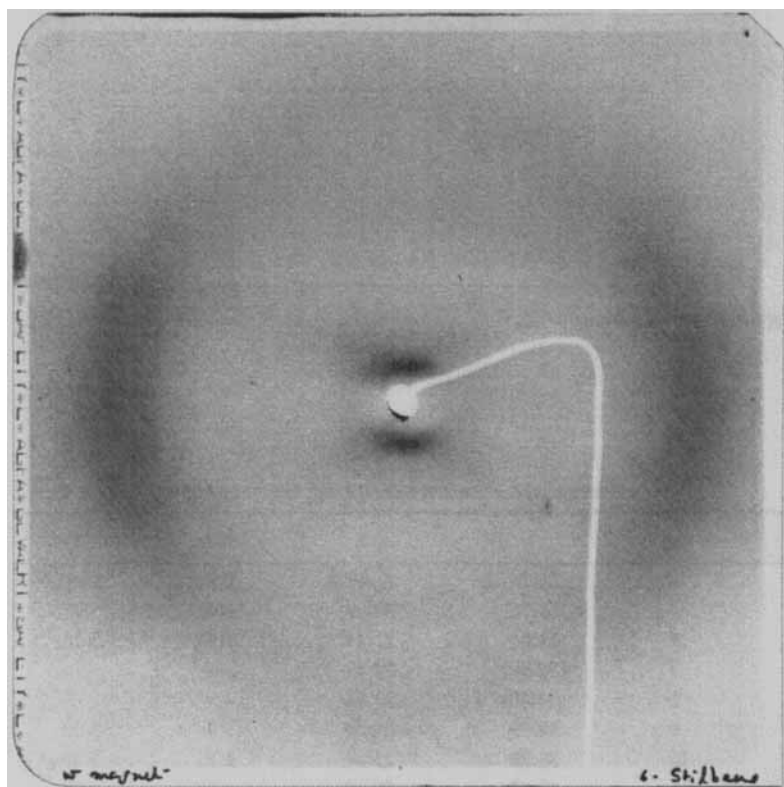


FIGURE 1 Normal-beam x-ray diffraction photographs of magnetically aligned 4-alkyl-4'-cyanostilbene. (Crystal monochromatized Fe $K\alpha$ radiation.)
(a) Nematic phase (hexyl); (b) Smectic-A phase (nonyl).

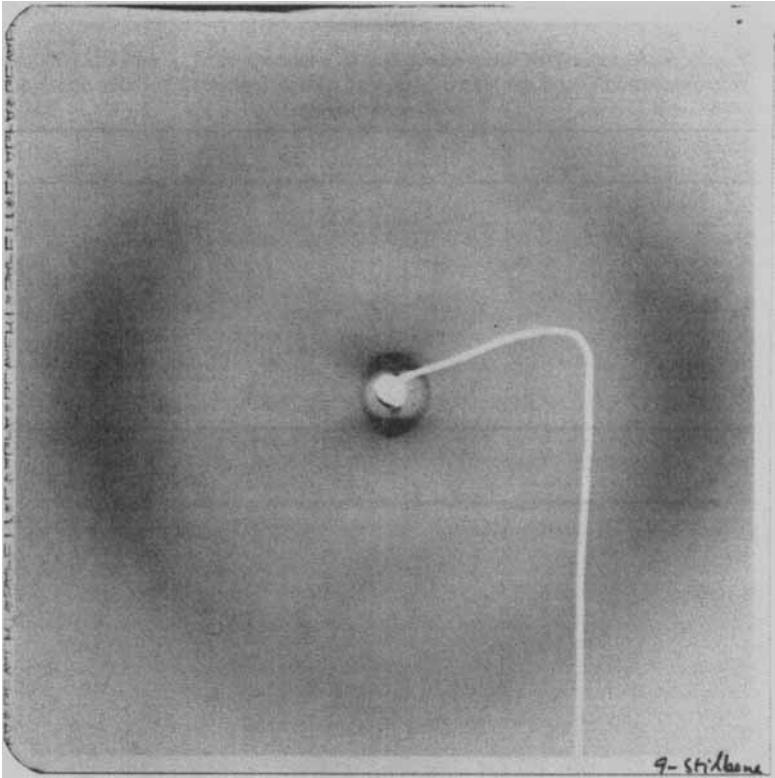


FIGURE 1 (continued)

TABLE 2
Comparison of measured and calculated spacings

<i>n</i>	<i>d</i>	<i>L</i>	<i>d/L</i>	<i>D</i>
4	26.77 Å	19.34 Å	1.38	5.16 Å
5	28.76	20.39	1.41	5.09
6	31.04	21.44	1.45	5.13
7	(32.39) ^a	22.49	—	—
8	(34.49) ^a	23.54	—	—
9	36.59	24.59	1.49	5.12
10	38.78	25.64	1.51	5.10
11	40.82	26.69	1.53	5.18

^aSince samples for *n* = 7 and 8 were not available, these values were interpolated assuming an incremental length of 1.05 Å per CH₂ group added.

to-side spacing D is more difficult to discern because of the breadth of the equatorial arcs.

The mean incremental length of the inter-layer spacing is 1.05 Å per methyl group added which suggests that the methyl chain forms an angle of 34° with the long axis of the rigid core. This can be compared to 28° for *p*-*n*-alcoxybenzoic acid,⁷ 30° for *p*-*n*-alkoxycinnamic acid,⁸ and 29° for 4,4' di-*n*-alkyl azoxybenzene.⁹ Since these compounds have symmetrical alkyl chains on both sides of the aromatic core, the following model emerges for the smectic-A phases studied here. The aromatic cores pack with their long axis nearly normal to the smectic layers. The alkyl tails form an angle of 34° with this axis but are free to rotate about the layer normal. The relatively sharp meridional reflection 001 and the absence of higher-order 00 ℓ reflections suggests a highly regular (planar) array of the rigid cores but a considerably less regular electron density distribution at the inter-layer boundaries. The relatively large amount of arcing and the breadth of the equatorial reflection, plus the total absence of higher-order reflections, strongly supports a rather "loose" short-range order among the parallel molecules having chains pointing in opposite directions. (The diffraction photographs in Figure 1 have cylindrical symmetry about the magnetic field direction as verified by upper-level precession photographs.)

The dimeric alignment of parallel neighbors having oppositely directed alkyl chains appears to persist in the nematic phase as well. In fact, the existence of an inner reflection along the meridian (Figure 1b) clearly indicates a long-range correlation of nearly parallel dimers along the nematic director. There is no side-to-side correlation (layering) and, again, the electron density distribution along the director is fairly periodic for the aromatic cores and less so for the terminal portions (alkyl tails) since higher-order reflections are totally absent. The disk-like intensity distribution about the 001 reciprocal-lattice point is what one expects from parallel periodic chains having no interchain correlations.¹¹ The d/L ratio (Table 2) in the nematic phases declines slightly from that in the smectic phases due to the "looseness" of the nematic packing but provides supporting evidence for the relatively high degree of alignment attained.

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