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Conformational Variability of Alkenyl Liquid Crystals

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The compound 1-(4′-cyanocyclohexyl)-trans-4-(1-penten-5-yl)-cyclohexane is a member in a series of compounds showing liquid crystal properties. The compound crystallizes in two different crystal forms. The structure determinations by single crystal X-ray diffraction show different molecular conformations and different molecular packing for the two crystal forms. The single crystal data are (at −110°C): $C_{18}H_{29}N$, M_r = 259.4, (I) Orthorhombic, $P2_12_12_1$; a = 10.886 (1), b = 26.709 (3), c = 5.5657 (8) Å, V = 1618.3 Å^3; Z = 4; D_x = 1.06 g cm^{-3}, μ = 4.55 cm^{-1}, F(000) = 576, R = 0.038, Rw = 0.042 for 1562 observed reflections (CuKα, $2\theta_{max}$ = 150°) (II) Triclinic, $P\bar{1}$; a = 6.137 (1), b = 23.256 (4), c = 5.989 (1) Å, α = 90.07 (1), β = 111.19 (2), γ = 94.38 (1)°, V = 794.2 Å^3; Z = 2; D_x = 1.08 g cm^{-3}, μ = 4.64 cm^{-1}, F(000) = 288, R = 0.052, Rw = 0.079 for 2949 observed reflections (CuKα, $2\theta_{max}$ = 150°). The molecular packing in form I is a herringbone structure in which the molecules are arranged head-to-tail while the packing in form II is parallel with an head-to-head and tail-to-tail arrangement of the molecules. All 41 possible molecular conformations involving the four aliphatic bonds of the molecule have been investigated by molecular mechanics. The two conformations found in the two crystal forms correspond to the conformations with the lowest calculated energy. Our results support earlier findings reported by one of us which indicate that the bend/splay elastic ratio k_{33}/k_{11} of liquid crystals is not related with the length/width ratio (L/W) of individual molecules, but with L/W of molecular ensembles.

Keywords: Alkenyl liquid crystals, crystal structure, packing mesophases, molecules vs mechanics, conformation, ensembles

INTRODUCTION

The 1-(4′-cyanocyclohexyl)-trans-4-alkenyl-cyclohexane liquid crystal compounds have recently been introduced as liquid crystal materials.[1,2] The present compound, 1-(4′-cycanocyclohexyl)-trans-4-(1-penten-5-yl)-cyclohexane is one member of this group and is identified as $0d_4CC$. The nomenclature nd_mCC used in this series is

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that "n" is the number of carbon atoms beyond the double bond, "m" is the number of bonds between the double bond and the rigid core, and "CC" refers to the two cyclohexane rings. Most compounds in this series show wide nematic ranges and high nematic-isotropic transition temperatures, properties which are required for liquid crystal display (LCD) applications.[1] These properties occur due to the fact that the molecules contain a flexible aliphatic chain and a semi-rigid molecular segment of cyclohexyl rings.[3,4] However, unlike others in the series, $0d_4CC$ shows both a smectic B phase at a temperature range of 20.1°–37.0°C and a nematic phase at 37.0°–54.7°C.[1] The present results show that the compound also crystallizes in two different forms. These phenomena are not observed in the case of its isomer, $1d_3CC$.[1,4] Although no direct correlation exists between the occurrence of different mesophases on one hand and different crystal forms on the other hand, it still is possible that a study of the two crystal forms may yield information regarding the two liquid crystal phases of the compound. Also, the molecular packing, observed in the two crystal structures, may suggest the organization which occurs in the mesophases. In addition to the crystal structures, studies on the exploration of all molecular conformations of the alkenyl side chain have been made. This study may improve the understanding of liquid crystalline behaviour of the compound since its molecular shape is related to the physical properties especially the elastic constants and viscosity.[2] The results may establish molecular design criteria to find new materials with improved properties for applications.

EXPERIMENTAL

Crystallization

Colorless single crystals of the two crystal forms were obtained from solvent evaporation at −10°C. Dichloromethane/methanol yields parallelopiped shaped crystals (Form I) while ether/hexane gives plate-like crystals (Form II). The crystals were unstable at room temperature. The crystals were mounted under cold N_2.

X-ray Diffraction

The X-ray diffraction data for both crystal forms were measured on a CAD4 diffractometer with Ni-filtered CuKα radiation (CuKᾱ, λ = 1.54178 Å) at −110(1)°C. Lattice parameters were calculated using 48 and 50 reflections ($15° < \theta < 30°$) for Form I and Form II respectively. The ω-2θ scan technique was employed and the 2θ range for data collections was 1.0°–150.0°. Three intensities control monitors were measured every 7200 seconds of X-ray exposure time and three orientational control reflections were checked every 200 reflections. Other experimental parameters are listed in Table I together with lattice information. Lorentz-polarization corrections were applied. No absorption correction was made. The structures were solved by the direct methods using the program MITHRIL[5] and refined by the program SHELX76.[6] The weighting function used was $1/\sigma^2(F)$. Nonhydrogen atoms were refined anisotropically. All hydrogens were located from successive difference Fourier syntheses, and refined isotropically.

TABLE I

Structural information and experimental parameters.

	Form I	Form II
Formula	$C_{18}H_{29}N$	$C_{18}H_{29}N$
Formula weight	259.4	259.4
Space group	$P2_12_12_1$	$P\bar{1}$
Unit Cell dimensions a(Å)	10.886(1)	6.137(1)
b(Å)	26.709(3)	23.256(4)
c(Å)	5.5657(8)	5.989(1)
α		90.07(1)
β		111.19(2)
γ		94.38(1)
V(Å^3)	1618.3	794.2
Z	4	2
Calculated density (g cm^{-3})	1.06	1.08
F(000)	576	288
μ (cm^{-1})	4.55	4.64
Crystal dimensions (mm)	0.15 x 0.30 x 0.40	1.0 x 0.8 x 0.2
Scan angle (°)	0.80+0.20tanθ	0.80+0.20tanθ
Aperture width (mm)	3.00+0.86tanθ	3.00+0.86tanθ
Scan time for a single reflection (s)	90	60
Variations of intensity monitors	0.021(5)	0.073(13)
Total number of reflections measured	1978	3595
Unique reflections	1951	3281
Observed reflections	1562 ($>3\sigma(F_o)$)	2949 ($>4\sigma(F_o)$)
Final R	0.038	0.052
Rw	0.042	0.079
Δ/esd in final refinement cycle		
nonhydrogen atoms	0.013	0.030
hydrogen atoms	0.012	0.029
Peaks in final difference Fourier map (e/Å^3)		
maximum	0.18	0.26
minimum	-0.15	-0.22
EOF=$[\Sigma w(F_o-F_c)^2/(N-NP)]^{1/2}$	1.35	3.28
NP (number of parameters refined)	288	288
N (number of data used)	1562	2949

Molecular Mechanics Calculations

The two molecular structures obtained from the X-ray diffraction study were used as the starting geometries to minimize the steric energy using the program MM2.[7,8] The same program was used to minimize the 41 unique conformations involving the four carbon-carbon bonds of the alkenyl side-chain.

RESULTS AND DISCUSSION

Crystal Structures

The atomic coordinates and isotropic equivalent thermal parameters for the two crystal forms are listed in Table II. Figure 1 shows a stereoview[9] and atomic numbering for the two molecules in the two structures, next to one another. Table III contains all the bond distances, between nonhydrogen atoms. Tables of bond angles, anisotropic thermal parameters for nonhydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and observed and calculated structure factors will be deposited.

The two molecules in the two crystal structures have similar bond distances and bond angles. The largest difference in bond length is 0.016 Å for C(8)–C(9). Both structures have the same conformation for the cyano group (*e*) and also the two cyclohexane groups are bonded together with the same conformation (*e*—*e*). The major differences occur in the torsional angles of the four aliphatic bonds and they are listed in Table IV for both Form I and Form II. Neither of the two molecules can be considered linear while there is a distinct bend for Form II (Figure 1).

Molecular Packing

Figures 2 and 3 show stereoviews of the molecular packing of Forms I and II respectively. It is interesting that both forms have different arrangements of the molecules. Form I shows a herringbone of head-to-tail molecular layers while in Form II all molecules are parallel to one another and form head-to-head and tail-to-tail molecular layers. The densities of the two Forms are slightly different, 1.06 and 1.08 g/cm^3 for I and II, respectively, and this is reflected in the fact that in Form II more intermolecular contacts are observed.

The herringbone pattern found in Form I is similar to that found in its isomer $1d_3$CC.[4] It was suggested that the angle between the long axes of the $1d_3$CC molecules in the adjacent stacks was sufficiently large (120°) to be considered as nearly parallel and that a nematic phase formation could occur from this crystal precursor. This conclusion might be acceptable since the nematic phase for $1d_3$CC occurs in a rather high temperature range of 79.4°–99.7°C.[1] However, even though $0d_4$CC shows a similar herringbone packing with a similar angle (120°, see Figure 2) between the long axes of the molecules in adjacent stacks, it forms both smectic and nematic mesophases at a lower temperature (20.1°–37.0°C and 37.0°–54.7°C, respectively). It may be proposed, therefore, that for $0d_4$CC the thermal energy is sufficient only to allow molecular motion within the layers and translational motion of the layers relative to one another, maintaining the layer character as in

TABLE II

Atomic Parameters. E.s.d.'s are within parentheses.

Form I				
Atom	x	y	z	U(EQ)*
C(1)	0.4190(2)	0.19023(7)	0.6178(4)	0.0209(6)
C(2)	0.3028(2)	0.22252(8)	0.6180(5)	0.0250(7)
C(3)	0.3005(2)	0.26110(8)	0.8196(5)	0.0258(7)
C(4)	0.4126(2)	0.29555(7)	0.8187(4)	0.0226(6)
C(5)	0.5279(2)	0.26332(8)	0.8261(5)	0.0246(6)
C(6)	0.5320(2)	0.22453(8)	0.6251(5)	0.0253(7)
C(7)	0.4061(2)	0.33340(8)	1.0234(4)	0.0258(7)
C(8)	0.5103(2)	0.37159(8)	1.0268(5)	0.0295(7)
C(9)	0.4961(2)	0.41128(9)	1.2247(5)	0.0313(7)
C(10)	0.3849(2)	0.44309(8)	1.1900(5)	0.0349(8)
C(11)	0.2965(3)	0.4491(1)	1.3489(7)	0.054(1)
C(1')	0.4230(2)	0.15418(7)	0.4008(4)	0.0214(6)
C(2')	0.3106(2)	0.11939(8)	0.3901(5)	0.0278(7)
C(3')	0.3130(2)	0.08528(8)	0.1693(5)	0.0279(7)
C(4')	0.4310(2)	0.05429(7)	0.1614(4)	0.0272(6)
C(5')	0.5451(2)	0.08808(9)	0.1734(5)	0.0291(7)
C(6')	0.5398(2)	0.12197(8)	0.3945(5)	0.0272(7)
C(7')	0.4336(2)	0.02363(8)	-0.0596(4)	0.0307(7)
N(8')	0.4349(2)	0.00169(7)	-0.2355(4)	0.0399(7)
Form II				
C(1)	0.5495(2)	0.29027(5)	0.1937(2)	0.0245(4)
C(2)	0.7181(2)	0.24243(5)	0.2334(2)	0.0278(4)
C(3)	0.6732(2)	0.20592(5)	0.0065(2)	0.0282(4)
C(4)	0.4202(2)	0.17900(5)	-0.1021(2)	0.0262(4)
C(5)	0.2536(2)	0.22684(5)	-0.1456(2)	0.0284(4)
C(6)	0.2965(2)	0.26335(5)	0.0806(2)	0.0281(4)
C(7)	0.3816(2)	0.14287(5)	-0.3285(2)	0.0307(4)
C(8)	0.1356(2)	0.11299(5)	-0.4438(2)	0.0314(4)
C(9)	0.1068(2)	0.07614(6)	-0.6643(3)	0.0360(5)
C(10)	-0.1339(2)	0.04751(6)	-0.7926(3)	0.0408(5)
C(11)	-0.3187(3)	0.05097(7)	-0.7345(3)	0.0499(6)
C(1')	0.5900(2)	0.32541(5)	0.4254(2)	0.0239(4)
C(2')	0.4232(2)	0.37358(5)	0.3869(2)	0.0277(4)
C(3')	0.4588(2)	0.40723(5)	0.6184(2)	0.0287(4)
C(4')	0.7143(2)	0.43262(5)	0.7363(2)	0.0270(4)
C(5')	0.8845(2)	0.38519(5)	0.7757(2)	0.0281(4)
C(6')	0.8436(2)	0.35197(5)	0.5425(2)	0.0272(4)
C(7')	0.7529(2)	0.46137(5)	0.9682(2)	0.0302(4)
N(8')	0.7846(2)	0.48133(5)	1.1534(2)	0.0388(4)

* $U(EQ) = 1/3\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$

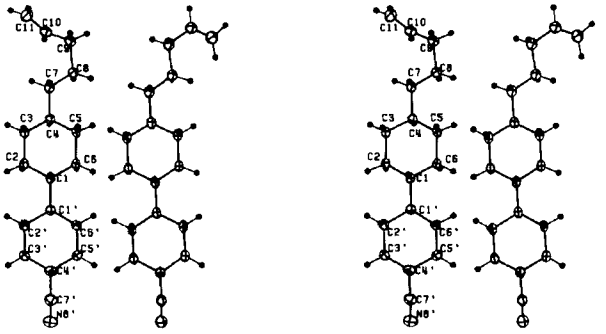

FIGURE 1 Stereoview and atomic numbering for the molecule of Form I (left) and Form II (right).

TABLE III

Bond distances. E.s.d.'s are within parentheses.

	Form I	Form II
N(8')-C(7')	1.141(3)	1.146(1)
C(7')-C(4')	1.478(3)	1.472(1)
C(4')-C(5')	1.537(3)	1.537(2)
C(4')-C(3')	1.529(3)	1.537(2)
C(5')-C(6')	1.529(4)	1.525(1)
C(6')-C(1')	1.536(3)	1.536(2)
C(1')-C(2')	1.537(3)	1.537(2)
C(2')-C(3')	1.530(4)	1.528(1)
C(1')-C(1)	1.545(3)	1.540(1)
C(1)-C(2)	1.531(3)	1.537(2)
C(1)-C(6)	1.534(3)	1.534(2)
C(2)-C(3)	1.524(3)	1.528(1)
C(3)-C(4)	1.529(3)	1.531(2)
C(4)-C(5)	1.523(3)	1.527(2)
C(5)-C(6)	1.525(3)	1.526(1)
C(4)-C(7)	1.525(3)	1.528(1)
C(7)-C(8)	1.526(3)	1.525(2)
C(8)-C(9)	1.537(4)	1.521(2)
C(9)-C(10)	1.491(4)	1.498(2)
C(10)-C(11)	1.317(5)	1.309(2)

a smectic phase. Only when temperature is further increased, will the molecules have sufficient energy to move parallel to one another with the result that the layer character vanishes. As a consequence, a nematic phase without the layer character may occur at a higher temperature. A similar consideration for the transition from the smectic to the nematic phase is also given by Bryan.[10] The herringbone pattern with similar angle as in Form I is also found in the crystal packing of ethyl *p*-azoxybenzoate which shows a smectic mesophase.[11]

In Form II, molecular packing is parallel as required for a nematic arrangement. However, the packing also shows a layer structure which is required for a smectic

TABLE IV

Torsional angles of side-chain bonds and steric energies, E (kcal/mol), for different conformations (see text). For comparison, the angles for Form II are for the molecule related by a c.s. relative to the coordinates given in Table II.

$\phi^3{}_1$ = C(3)-C(4)-C(7)-C(8) $\phi^5{}_1$ = C(5)-C(4)-C(7)-C(8)

ϕ_2 = C(4)-C(7)-C(8)-C(9) ϕ_3 = C(7)-C(8)-C(9)-C(10)

ϕ_4 = C(8)-C(9)-C(10)-C(11)

	$\phi^3{}_1(\phi^5{}_1)$	ϕ_2	ϕ_3	ϕ_4	E	
Form I	-176.2(61.4)	176.0	-63.8	123.7		
Form II	-178.2(59.1)	178.3	177.5	0.1		
a	-174.7(63.9)	174.9	178.9	-116.5	19.30	
b	-175.3(63.2)	174.9	178.4	117.1	19.33	
c	-173.1(65.6)	174.2	62.9	-117.9	19.57	
d	-173.3(65.4)	176.8	-64.0	118.0	19.70	(I)
e	-174.6(63.9)	174.1	179.0	1.5	19.87	(II)
	-178.6(59.9)	57.8	58.5	-118.6	19.94	
	179.2(57.6)	56.9	176.9	-116.8	19.98	
	-174.6(64.0)	171.4	63.7	107.1	19.99	
	179.5(57.8)	57.4	177.0	116.0	19.99	
	61.9(-62.5)	-178.7	179.5	117.4	20.15	
	-172.0(66.7)	-180.0	-65.6	-106.2	20.22	

mesophase. Both types of mesophases can therefore be generated from this crystal form.

Smectic mesophases are characterized by a layer structure.[12] Although there is close similarity between the packing in Form I of $0d_4CC$ and its isomer $1d_3CC$, as described above, there is also a distinct difference. In the layers for $1d_3CC$ one can clearly see that adjacent molecules are not on top of another and interleafed (Figure 4b of reference 4), schematically indicated in Figure 4a; while for Form I of $0d_4CC$ adjacent molecules are packed quite closely on top of one another, schematically shown in Figure 4b. Another description is that the boundary between layers in Form I of $0d_4CC$ is smooth but that this boundary is ruffled in $1d_3CC$. In the latter case, therefore, the layers of molecules can not translate relative to one

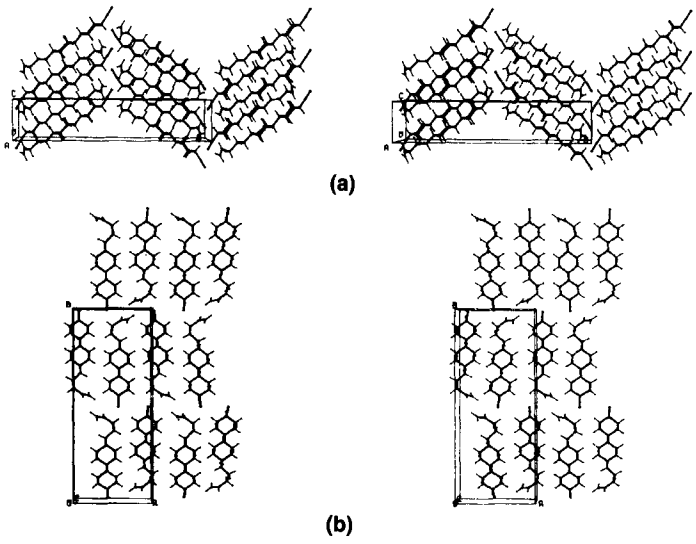

FIGURE 2 Stereoviews of molecular packing of Form I as seen down (a) the *a* axis and (b) the *c* axis.

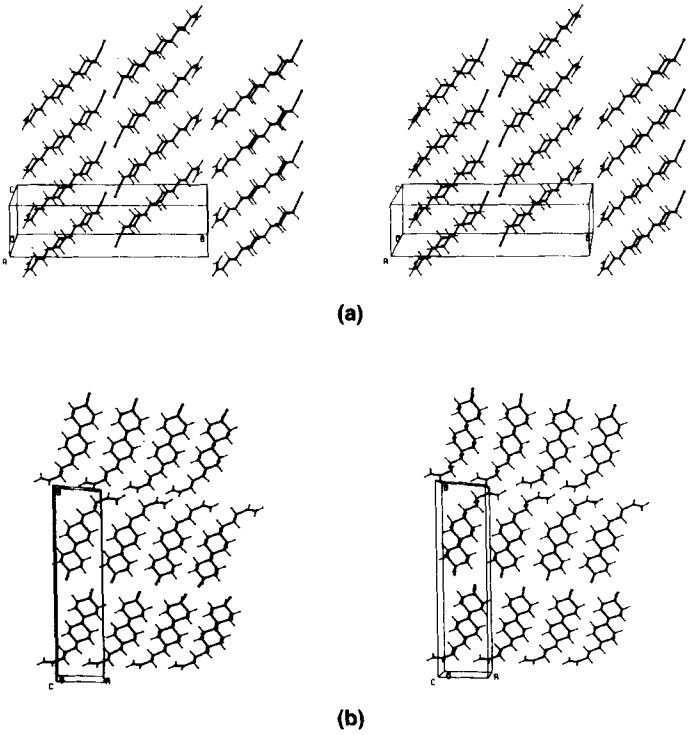

FIGURE 3 Stereoviews of molecular packing of Form II as seen down (a) the *a* axis and (b) the *c* axis.

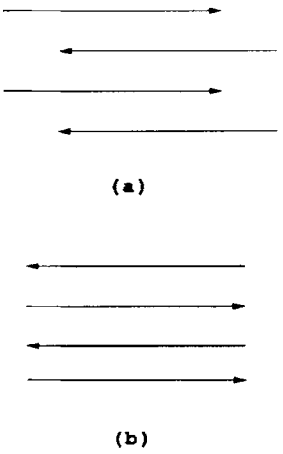

FIGURE 4 Schematic drawing for the packing within a layer for $1d_3CC$ (a) and $0d_4CC$ (b). The arrow head indicates the cyano group.

another, and this may be the cause that in $1d_3CC$ a smectic mesophase does not exist while it does occur for $0d_4CC$.

This difference in packing for Form I of $0d_4CC$ and $1d_3CC$ has another consequence which is that the length over width ratio (L/W) for an assembly of molecules would be larger for $1d_3CC$ than for $0d_4CC$. This experimental observation agrees with the results of an earlier modeling study made for the two compounds by Schadt and coworkers. From this study it was concluded that it is not the L/W ratio of individual molecules but the L/W ratio of molecular ensembles which is correlated with the splay/bend elastic ratio k_{33}/k_{11} of liquid crystals.[1] Our present results indicate the importance of combining molecular modeling and structural observations to study intermolecular interactions between adjacent molecules, primarily in directions perpendicular to the long axes of the molecules.

Conformational Analyses

There are four single bonds in the side chain of the molecule and a definition of the conformational angles for these bonds is given in Table IV. We find, as expected, three energy minima for each of these four angles by using the driver option in the MM2 program. These are trans (180°) or gauche ($\pm 60°$) for each of ϕ_1, ϕ_2, and ϕ_3 and 0° or $\pm 120°$ for ϕ_4. There is a total of 162 different conformations for the side chain. If one accepts that C(3) and C(5) are equivalent this reduces to 81. Also conformations related by a mirror plane are equivalent and thus the number reduces to 42. A number of these conformations are sterically impossible but all others have been energy-minimized. The results of these calculations show that there are a large number of low energy conformations: 19 with energy between 19.3 and 21 kcal. This large number of accessible conformations is probably important in the formation of mesophases and can possibly be related to order parameters observed in these phases. A listing of the eleven formations within 1 kcal from the lowest energy conformation is given in Table IV. The five conformations with the lowest energy are indicated by **a**, **b**, **c**, **d**, and **e**. Several conclusions can

be drawn from this information. There is a distinct preference for ϕ_1, to be 'gt' ($\phi_1^3 \sim 180°$ and $\phi_1^5 \sim -60°$) rather than 'gg' ($\phi_1^3 = 60°$ and $\phi_1^5 = -60°$). As a matter of fact only one of the eleven has this latter conformation. One can expect the 'gg' conformation, therefore, to be of no significance in mesophases. Also the barrier for the 'gt' → 'gg' conformational change is rather high (>4 kcal). Similar conclusions were made for $0d_3CC$ and $1d_3CC$[4] and cyanophenylcyclohexanes.[13] There is a preference for a trans conformation for ϕ_2 and this can be explained by steric effects as well. The driver calculation also shows an energetic preference for ϕ_2 to be ~180°. The occurrence of a 'g'-conformation for ϕ_2 in a mesophase may require a concerted change in one of the other conformational angles. Most of the freedom is in ϕ_3 as can be seen from the results in Table IV. For ϕ_4 there is a distinct preference for the angle to be $\pm 120°$ rather than 0° and this is also obvious from the results of the driver calculation.

Table IV lists in the top two lines the conformational angles found in the two crystal structures for $0d_4CC$. It is clear that conformations **d** and **e** are the same as those found in the crystal structures, Form I and II, respectively and it is interesting to note, therefore, that neither of the two crystal structures contain the lowest energy conformation for the isolated molecule and packing forces must be the cause for that observation. The two lowest energy conformations for the isolated molecule are related to **e** (and crystal Form II) by adopting the more favorable and similar $\pm 120°$ conformations for ϕ_4. The conformation found in Form II (**e**) may be caused by intermolecular repulsions between the tails of neighboring molecules (Figure 3). Conformation **c** is distinct from the other low-energy conformations. The results of the conformational analysis show, therefore, quite clearly that both the energy of the conformer and the intermolecular interaction determine the crystal structures which are observed and that additional conformations beyond those found in crystal structures need to be considered for mesophases.

In conclusion, we found two crystal forms for $0d_4CC$ with different molecular conformations and packings. Both forms have a layer structure which is one of the characteristics of the smectic arrangement. From an investigation of conformation variability, we conclude that the isolated molecule possesses several conformations with relatively low energy. However, in the crystalline state only two of those conformations appear. The conformations found in the crystal structure will give information about molecular structural parameters such as length over width ratios which are related to bend over splay elastic constants.[1,14,15] and suitable properties of LCD applications such as multiplexibility and short electro-optical response times may be determined from these constants.[1]

SUPPLEMENTARY MATERIAL

Anisotropic thermal parameters, hydrogen atomic parameters, and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. 90266. Copies may be obtained through Customer Services, The British Library, Document Supply Centre, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, United Kingdom.

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