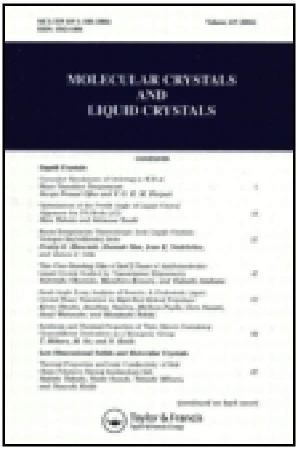

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The Crystal and Molecular Structures of Two 4-Alkenyl-substituted Bicyclohexylnitriles

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The Crystal and Molecular Structures of Two 4-Alkenyl-substituted Bicyclohexylnitriles

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The crystal and molecular structures of two mesomorphic alkenyl bicyclohexylnitriles have been studied by single-crystal X-ray diffraction and molecular mechanics. 1-(4′-cyanocyclohexyl)-*trans*-4-(1-buten-4-yl)-cyclohexane (**0d$_3$CC**): monoclinic, $P2_1/c$; a = 6.415(1), b = 20.453(5), c = 22.998(7) Å, β = 94.99(3)°, V = 3006.0 Å^3; Z = 8; R = 0.035, Rw = 0.039 for 4509 reflections with $I_0 \geq 2\sigma\ (I_0)$. 1-(4′-cyanocyclohexyl)-*trans*-4-(2-penten-5-yl)-cyclohexane (**1d$_3$CC**): monoclinic, $P2_1/n$; a = 5.418(1), b = 31.992(7), c = 9.380(2) Å, β = 101.93(2)°, V = 1590.7 Å^3; Z = 4; R = 0.063, Rw = 0.057 for 1613 reflections with $I_0 \geq 2\sigma\ (I_0)$. The molecular structures are discussed with regard to the torsional angles around the C(4)—C(7) bond connecting the cyclohexane ring and the flexible chain in each of the molecules. A scan in the conformational space around the C(4)—C(7) bond, using the molecular mechanics, program MM2, reveals that the two different conformations, which the two molecules assume in their crystal structures, are energetically equivalent. **0d$_3$CC** shows a parallel imbrication of molecules in the crystal, which yields a nematic mesophase. On the other hand, **1d$_3$CC** displays a herringbone relationship on molecular stacks in the crystal structure, but it still yields a nematic mesophase as well.

INTRODUCTION

The title compounds are two of a number of recently introduced 1-(4′-cyanocyclohexyl)-*trans*-4-alkyl-cyclohexane liquid crystal materials.[1,2] In these and other bicyclohexyl alkenyls, the position of the double bond in the alkenyl side chain affects the elastic constants and the rotational viscosity considerably.[1,2] The wide range of material properties makes these alkenyl liquid crystals suitable materials for virtually all LCD applications, including TN-LCD, OMI-LCD, and STN-LCD.

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TABLE I

Structural information and experimental parameters

	$0d_3CC$	$1d_3CC$
Formula	$C_{17}H_{27}N$	$C_{18}H_{29}N$
Formula weight	245.41	259.44
Space group	$P2_1/c$	$P2_1/n$
Unit Cell dimensions a(Å)	6.415(1)	5.418(1)
b(Å)	20.453(5)	31.992(7)
c(Å)	22.998(7)	9.380(2)
β(°)	94.99(3)	101.93(2)
V(Å^3)	3006.0	1590.7
Z	8	4
Calculated density (g cm^{-3})	1.08	1.08
F(000)	1088	576
μ (cm^{-1})	3.94	3.92
Data Crystal volume (mm^3)	0.17 x 0.20 x 0.43	0.23 x 0.10 x 0.07
Data Collection range h	-8 to 8	-6 to 6
k	0 to 25	0 to 40
l	0 to 28	0 to 11
Scan angle (°)	$0.80 + 0.20\tan\theta$	$0.90 + 0.20\tan\theta$
Aperture width (mm)	$2.00 + 0.86\tan\theta$	$3.50 + 0.86\tan\theta$
Scan time for a single reflection (s)	60	90
Variations of intensity monitors	0.027(7)	0.032(6)
Total number of reflections measured	6582	3508
Unique reflections	6158	3275
Observed reflections [$I \geq 2\sigma(Io)$]	4509	1613
Final R	0.035	0.063
Rw	0.039	0.057
Δ/esd in final refinement cycle		
nonhydrogen atoms	≤ 0.044	≤ 0.031
hydrogen atoms	≤ 0.061	≤ 0.028
Peaks in final difference Fourier map (e/Å^3)		
maximum	0.25	0.26
minimum	-0.15	-0.27
EOF = $[\Sigma w(Fo-Fc)^2/(N-NP)]^{1/2}$	1.5	1.4
NP (number of parameters refined)	542	288
N (number of data used)	4509	1613

TABLE II

Atomic parameters

(a) **0d$_3$CC**

Atom	X	Y	Z	U(EQ)*
N(8')A	0.6751(2)	0.93665(6)	0.02922(5)	0.0392(4)
C(7')A	0.5157(2)	0.93854(6)	0.04815(6)	0.0304(4)
C(4')A	0.3152(2)	0.94057(6)	0.07528(6)	0.0269(4)
C(5')A	0.3032(2)	1.00225(6)	0.11296(6)	0.0271(4)
C(6')A	0.1018(2)	1.00284(6)	0.14411(6)	0.0260(4)
C(1')A	0.0792(2)	0.94224(6)	0.18227(5)	0.0224(4)
C(2')A	0.0938(2)	0.88086(6)	0.14417(6)	0.0293(4)
C(3')A	0.2928(2)	0.87874(6)	0.11220(6)	0.0290(4)
C(1)A	-0.1229(2)	0.94314(6)	0.21403(5)	0.0224(4)
C(2)A	-0.1433(2)	0.88171(6)	0.25135(6)	0.0286(4)
C(3)A	-0.3386(2)	0.88200(6)	0.28477(6)	0.0268(4)
C(4)A	-0.3536(2)	0.94241(6)	0.32314(5)	0.0232(4)
C(5)A	-0.3351(2)	1.00393(6)	0.28622(6)	0.0257(4)
C(6)A	-0.1388(2)	1.00375(6)	0.25270(6)	0.0261(4)
C(7)A	-0.5547(2)	0.94028(6)	0.35436(6)	0.0260(4)
C(8)A	-0.5821(2)	0.99588(7)	0.39759(6)	0.0310(4)
C(9)A	-0.7717(2)	0.98617(7)	0.43036(6)	0.0330(4)
C(10)A	-0.9416(2)	1.02256(9)	0.42457(7)	0.0415(5)
N(8')B	-1.7196(2)	0.84015(6)	0.59929(5)	0.0425(4)
C(7')B	-1.5643(2)	0.82991(7)	0.58019(6)	0.0308(4)
C(4')B	-1.3664(2)	0.81548(6)	0.55431(6)	0.0263(4)
C(5')B	-1.3651(2)	0.84698(6)	0.49380(6)	0.0264(4)
C(6')B	-1.1625(2)	0.83049(6)	0.46617(6)	0.0265(4)
C(1')B	-1.1271(2)	0.75659(6)	0.46143(5)	0.0224(4)
C(2')B	-1.1311(2)	0.72608(7)	0.52238(6)	0.0271(4)
C(3')B	-1.3328(2)	0.74134(6)	0.55049(6)	0.0287(4)
C(1)B	-0.9252(2)	0.73892(6)	0.43312(5)	0.0224(4)
C(2)B	-0.9007(2)	0.66481(6)	0.42605(6)	0.0276(4)

TABLE II (*continued*)

C(3)B	-0.7043(2)	0.64629(6)	0.39685(6)	0.0272(4)
C(4)B	-0.6937(2)	0.67878(6)	0.33728(5)	0.0236(4)
C(5)B	-0.7158(2)	0.75267(6)	0.34412(6)	0.0262(4)
C(6)B	-0.9122(2)	0.77176(6)	0.37352(6)	0.0260(4)
C(7)B	-0.4920(2)	0.65916(7)	0.31045(6)	0.0275(4)
C(8)B	-0.4689(2)	0.68452(7)	0.24886(6)	0.0318(4)
C(9)B	-0.2860(2)	0.65394(7)	0.22262(6)	0.0324(4)
C(10)B	-0.1236(2)	0.68416(9)	0.20503(7)	0.0412(5)

(b) **$1d_3CC$**

Atom	X	Y	Z	U(EQ)*
N(8')	-0.1796(7)	0.2697(1)	0.9140(4)	0.042(1)
C(7')	-0.0108(8)	0.2488(1)	0.9105(4)	0.030(1)
C(4')	0.1951(8)	0.2197(1)	0.9014(4)	0.029(1)
C(5')	0.1747(9)	0.2063(1)	0.7424(4)	0.035(2)
C(6')	0.3737(9)	0.1741(1)	0.7268(5)	0.035(2)
C(1')	0.3609(7)	0.1352(1)	0.8206(4)	0.025(1)
C(2')	0.3870(8)	0.1493(1)	0.9795(4)	0.030(1)
C(3')	0.1894(8)	0.1816(1)	1.0005(5)	0.031(1)
C(1)	0.5522(7)	0.1015(1)	0.8025(4)	0.025(1)
C(2)	0.5217(8)	0.0616(1)	0.8871(4)	0.028(1)
C(3)	0.7069(8)	0.0269(1)	0.8676(4)	0.030(1)
C(4)	0.6847(7)	0.0151(1)	0.7081(4)	0.026(1)
C(5)	0.7204(8)	0.0545(1)	0.6224(4)	0.030(1)
C(6)	0.5386(8)	0.0897(1)	0.6428(4)	0.028(1)
C(7)	0.8721(8)	-0.0189(1)	0.6863(5)	0.029(1)
C(8)	0.8350(8)	-0.0616(1)	0.7531(5)	0.031(1)
C(9)	1.0305(7)	-0.0926(1)	0.7310(4)	0.030(1)
C(10)	0.9852(8)	-0.1309(1)	0.6769(4)	0.029(1)
C(11)	1.1844(9)	-0.1615(1)	0.6568(5)	0.037(2)

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

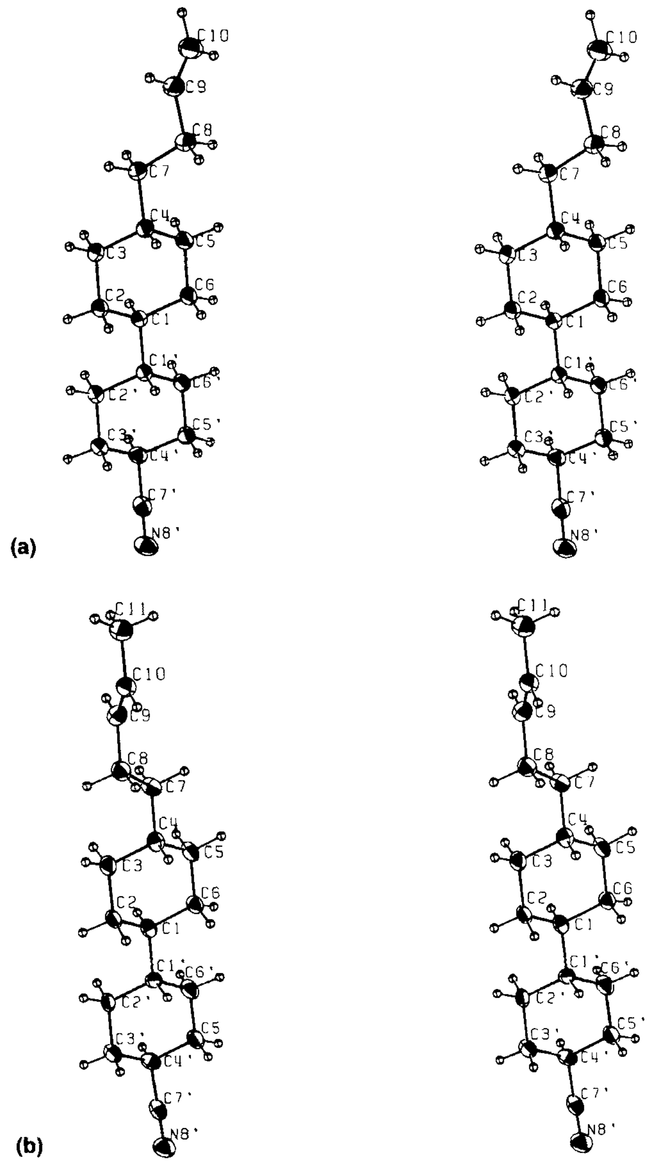

FIGURE 1 Stereoviews with atomic numbering scheme for (a) molecule **A** of **0d$_3$CC** and (b) a single molecule of **1d$_3$CC**.

TABLE III

Bond distances with e.s.d.'s in parentheses

	$0d_3CC$		$1d_3CC$
	A	B	
N(8')-C(7')	1.147(2)	1.142(2)	1.140(5)
C(7')-C(4')	1.478(2)	1.478(2)	1.467(6)
C(4')-C(5')	1.536(2)	1.534(2)	1.534(5)
C(4')-C(3')	1.537(2)	1.535(2)	1.539(5)
C(5')-C(6')	1.531(2)	1.533(2)	1.520(6)
C(6')-C(1')	1.533(2)	1.534(2)	1.533(5)
C(1')-C(2')	1.538(2)	1.537(2)	1.535(4)
C(1')-C(1)	1.542(2)	1.542(2)	1.530(5)
C(2')-C(3')	1.528(2)	1.528(2)	1.528(6)
C(1)-C(2)	1.534(2)	1.534(2)	1.531(5)
C(1)-C(6)	1.534(2)	1.535(2)	1.532(4)
C(2)-C(3)	1.525(2)	1.526(2)	1.532(6)
C(3)-C(4)	1.526(2)	1.529(2)	1.523(4)
C(4)-C(5)	1.528(2)	1.527(2)	1.527(5)
C(4)-C(7)	1.531(2)	1.535(2)	1.532(6)
C(5)-C(6)	1.532(2)	1.531(2)	1.534(6)
C(7)-C(8)	1.531(2)	1.528(2)	1.532(5)
C(8)-C(9)	1.499(2)	1.502(2)	1.497(6)
C(9)-C(10)	1.317(2)	1.306(2)	1.329(5)
C(10)-C(11)			1.497(6)

For these compounds, the nomenclature nd_mCC is commonly used. "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. Accordingly, 1-(4′-cyanocyclohexyl)-*trans*-4-(1-buten-4-yl)-cyclohexane is named as **0d$_3$CC**, and 1-(4′-cyanocyclohexyl)-*trans*-4-(2-penten-5-yl)-cyclohexane, **1d$_3$CC**.

The orientational order of this type of liquid crystals has been investigated by using natural abundance ^{13}C NMR spectroscopy.[3] However, it proves difficult to describe the detailed ordering of the chain because of its flexibility. The single crystal structures for these compounds may yield information on how the liquid

TABLE IV

Torsion angles along the chain, C(4) through C(9)

	0d$_3$CC			1d$_3$CC		
	1* (A/B)	2**	3***	1*	2**	3***
C(3)-C(4)-C(7)-C(8)	176°/176°	173°	64°	65°	65°	175°
C(4)-C(7)-C(8)-C(9)	−174°/−170°	−174°	174°	−178°	177°	−179°
C(7)-C(8)-C(9)-C(10)	−112°/−120°	−115°	−117°	−129°	−120°	−116°
Steric Energy (kcal/mol)		18.7	18.7		18.5	18.6

1* Crystal structure.
2** Minimized crystal structure (MM2).
3*** Energetically equivalent conformer, minimized.

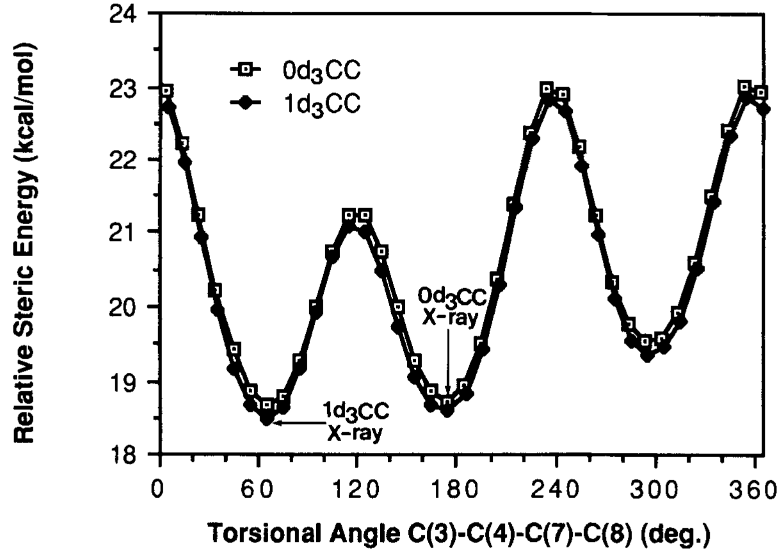

FIGURE 2 Plot of the MM2 energy profile versus the torsional angle C(3)–C(4)–C(7)–C(8) for **0d$_3$CC** and **1d$_3$CC**. Also shown is the crystallographic values.

crystal phases can be obtained. Especially the conformations of the molecules and the molecular packing are of interest. Molecular mechanics is widely used to study molecular conformations, with which different conformers can be evaluated energetically. Therefore, single crystal X-ray diffraction and molecular mechanics

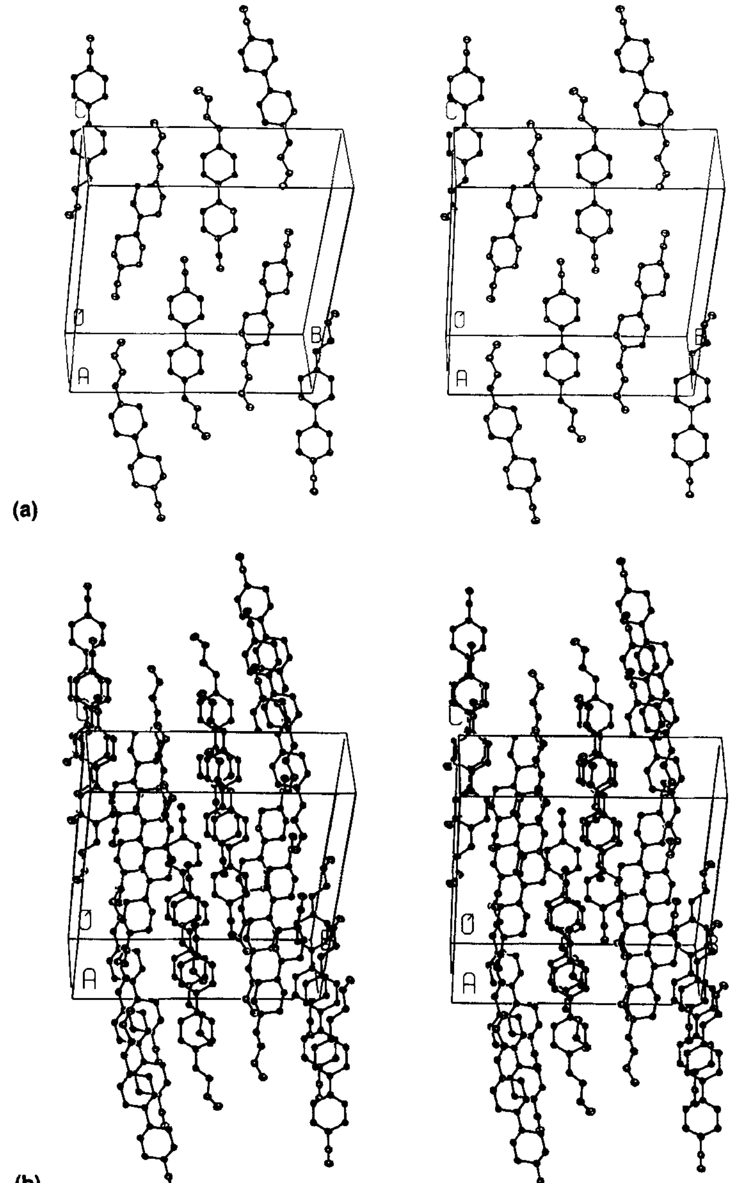

FIGURE 3 (a) One layer and (b) multilayer of **0d$_3$CC** molecules with the unit cell orientation.

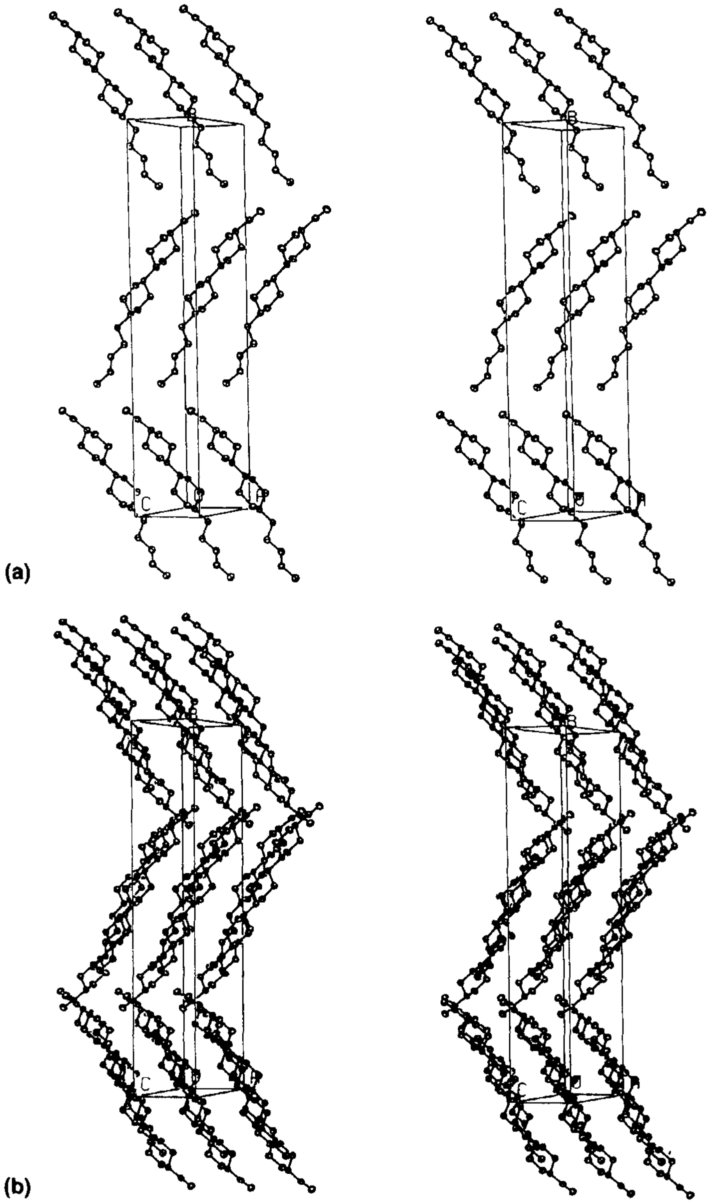

FIGURE 4 (a) One layer and (b) multilayer of **1d$_3$CC** molecules with the unit cell orientation.

were carried out for **$0d_3CC$** and **$1d_3CC$**, for both of which suitable crystals were available.

EXPERIMENTAL

X-ray Diffraction

The X-ray diffraction data were measured on a CAD4 diffractometer with Ni-filtered CuKα radiation (CuKα, $\lambda = 1.54178$ Å) at $-110(1)$°C. 48 reflections ($15° < \theta < 30°$) and CuKα_1 wavelength (1.54051 Å) were used to calculate lattice parameters. The ω-2θ scan technique was employed and the 2θ range for data collection was 1.0° – 150.0°. Three intensity control monitors were measured every 7200 seconds of X-ray exposure time and three orientation 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 using the direct methods program SHELXS-86.[4] The structures were refined by SHELX76[5] and 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.

Molecular Mechanics Calculations

Molecular mechanics calculations were carried out by using the program MM2.[6] The strain energy of **$0d_3CC$** and **$1d_3CC$** was minimized while using the crystal coordinates as the starting geometry. Rotation around C(4)–C(7) in both compounds was carried out by driving the torsional angle in 10° increments while relaxing all other angles.

RESULTS AND DISCUSSION

There are two independent molecules, **A** and **B**, in the asymmetric unit in the **$0d_3CC$** crystal structure, and one for **$1d_3CC$**. The final coordinates and isotropic equivalent thermal parameters are listed in Table II. Figure 1 shows stereoviews[7] for the **$0d_3CC$** and **$1d_3CC$** molecules. 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 (43 pages) will be deposited.

The three molecules, **A** and **B** of **$0d_3CC$** and the **$1d_3CC$** molecule, have very similar bond distances and bond angles. No unusual bond length is observed. The only difference in bond length which is larger than 3σ is 0.023 Å for C(9)=C(10). The thermal C(9)=C(10) bond in **$0d_3CC$** is shorter than the nonterminating double bond in **$1d_3CC$** due to the fact that this double bond interacts with one single bond in **$0d_3CC$**, but with two in **$1d_3CC$**. The $C(7')_{sp}$–$C(4')_{sp^3}$ bond is shorter than the

$C(10)_{sp^2}$–$C(11)_{sp^3}$ bond, as expected, and also, both are shorter than other C_{sp^3}–C_{sp^3} bonds.

Steric energy minimization, using the program MM2,[5] shows that both structures are close to their energy minima. This can be seen from the torisional angles along the flexible chain (Table IV), among which the largest difference between the crystal structure and minimized crystal structure is only 9° for the angle C(8)–C(9) in **1d$_3$CC**. The major difference in the conformation for **0d$_3$CC** and **1d$_3$CC** is the conformation around C(4)–C(7) (≈110°, Table IV). The largest flexibility in this type of molecule appears to exist in the conformational space around the C(4)–C(7) bond. The conformational scan around this bond results in three energy minima separated by two barriers, in both **0d$_3$CC** and **1d$_3$CC** (Figure 2). The first two minima are energetically equivalent (see also Table IV) and are separated by an energy barrier of 21.2 kcal/mol. The third minimum has an energy higher than the first two by 1.0 kcal/mol, and is separated from the first two by a barrier of 23.0 kcal/mol. These observations are consistent with the results obtained from the method of the potential of mean torque applied to the chain ordering in phenylcyclohexanes.[8] (Only three conformations due to rotations about the C(4)–C(7) bond are allowed. Two of these rotamers are equivalent to each other. The third one is higher in energy than the first two.) It is noted that the two energetically equivalent conformers for this type of molecule, predicted both by molecular mechanics and other theoretical calculations, are found in the crystal structures of **0d$_3$CC** and **1d$_3$CC**.

There are no unusual intermolecular distances in both compounds. Both **0d$_3$CC** and **1d$_3$CC** form molecular layers in their crystals, but the arrangement of molecules in the layer and the orientation of the layer with respect to the crystal lattice are different in the two compounds (Figure 3 and 4). **0d$_3$CC** shows a parallel imbrication of molecules in the crystal (Figure 3), which is considered as a necessary condition for the solid to yield a nematic mesophase.[9] **1d$_3$CC** displays, however, a herringbone relationship of molecular stacks in the crystal structure (Figure 4), which is known to prevent the mesophase formation in the case of trans-cinnamic acid.[9] Both **0d$_3$CC** and **1d$_3$CC**, however, yield nematic mesophases.[2] In the crystal structure of trans-cinnamic acid,[9] the long axes of molecules in adjacent stacks incline at 45°, whereas this angle for **1d$_3$CC** is 120°. It is concluded, therefore, that when the angle between the long axes of the molecules in adjacent stacks is large enough so that the long molecule axes in adjacent stacks can be considered as nearly parallel, the herringbone relationship of molecular stacks may not prevent the mesophase formation.

Recently, the equilibrium configuration of an ensemble of twelve **1d$_3$CC** molecules was calculated by using the Roche interactive molecular graphics program (RIMG).[2] Although there does not seem to be a direct correlation between the calculated equilibrium configuration and the crystal structure, a further investigation using the actual crystallographic data presented here and the order parameters obtained from NMR studies[3] in this kind of calculations may shed some light between the molecular structure and physical properties of the liquid crystalline phase.

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Supplementary Material

Supplementary material available by contacting Gordon & Breach at 5301 Tacony Street, Box 330, Philadelphia, PA 19137. Please mark your envelope Supplementary Materials.

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