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Structural analysis of a mesogenic 4-alkenyl bicyclohexylnitrile

SAKUNTALA GUPTA*, R. A. PALMER†, M. SCHADT‡
and S. P. SEN GUPTA

Department of Materials Science, Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700 032, India
†Department of Crystallography, Birkbeck College, Malet Street,
London WC1E 7HX, UK
‡Rolic Research Ltd., Gewerbestrasse 18. CH-4123 Allschwil, Switzerland

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The crystal and molecular structures of the mesomorphic compound having the molecular formula C_5H_9–C_6H_{10}–CN have been determined at 273 K. The compound crystallizes in a non-centrosymmetric orthorhombic system with the space group $P2_12_12_1$, and 4 molecules in the unit cell with cell dimensions $a = 5.656$ (1) Å, $b = 9.134$ (2) Å and $c = 31.001$ (6) Å. Both cyclohexyl rings adopt chair conformations and are nearly coplanar. With regard to the crystal packing, contacts between the polar cyano groups cannot be observed and the molecules are stacked along the *c*-axis. Imbricated packing is a precursor to nematogenic behaviour. The molecular packing and phase sequences of this compound are compared with two other related compounds. The effect of a double bond in specific terminal chain positions is discussed.

1. Introduction

The introduction of a double bond in specific positions along the terminal chain markedly affects the properties of the liquid crystalline homologous series, the 4-alkenyl bicyclohexylnitriles, Yd_xCC. The alkenyl double bond is denoted as d_x, where x designates the position of the double bond from the nearest cyclohexyl ring. Y is the number of carbon atoms beyond the double bond. As part of our programme to solve the structures of this homologous series, we have studied the crystal structure of 4-(1″-pentenyl)-4′-(cyano)-1,1′-bicyclohexane ($3d_1CC$). We have previously studied two other members, $1d_3CC$ and $1d_1CC$, and these structures have been reported elsewhere [1, 2]. The transition temperatures of $3d_1CC$ are [3]:

Cr–59.3–N–91.7–I (°C).

2. Experimental

2.1. *Crystal data*

$3d_1CC$ was prepared as described by Schadt *et al.* [3]. A single crystal of the compound was obtained from acetone solution by slow evaporation at 296 K. The size of the colourless block crystal was $0.5 \times 0.3 \times 0.2\,mm^3$. From the systematic absences of $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd, the space group is uniquely determined to be $P2_12_12_1$.

Accurate cell parameters have been determined at 273 K and refined by a least squares fit of $\sin\theta$ values of 25 reflections having θ values $38° < \theta < 45°$, measured on CAD-4 EXPRESS [4]. Data collection at 273 (2) K was done by CAD-4 EXPRESS having θ values $2.98° < \theta < 28.46°$. The index ranges are found to be $-4 \leqslant h \leqslant 7$, $-8 \leqslant k \leqslant 11$, and $-37 \leqslant l \leqslant 38$. Data reduction was done by XCAD-4 [5]. MoK_α radiation and a graphite monchromator were used to collect 3457 reflections in ω-2θ scan mode, of which 1979 were treated as observed with $I > 2\,\sigma(I)$.

2.2. *Structure determination and refinement*

The structure was solved using the UNIX version of SHELXS-97 [6]. From the E-map we could locate 19 non-hydrogen atoms. The structure thus obtained was refined by the full-matrix least squares method on F^2 using the UNIX version of SHELXL-97 [7] with an individual isotropic temperature factor to an R value of 0.13. Introduction of individual anisotropic temperature factors reduced the R value to 0.11. The positions of the hydrogen atoms were then inserted from the known geometry around the carbon atoms. The H atoms were

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*Author for correspondence;
e-mail: mssg@mahendra.iacs.res.in

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allowed to ride on their parent atom with U_{iso} (H) = xU_{eq} (parent), where $x = 1.5$ for methyl and $x = 1.2$ for all others. Hydrogen atoms were included in structure factor calculations but not refined. An extinction correction was applied and the extinction coefficient was 0.0056 (7). The atomic scattering factors were taken from the literature [8]. Finally we obtained an R-value of 0.052 and $R_w = 0.088$. A difference Fourier map at this stage showed no electron density greater than 0.147 e Å^{-3}. The Flack x parameter was 3 (5) and absolute structure could not be determined reliably [9]. Detailed crystal structure data of the solution and refinement are summarized in table 1. For molecular graphics the programme ZORTEP [10] was used.

Table 1. Summary of the crystal data of the solution and refinement.

Parameter	Value
Crystal data	
Molecular formula	$C_{18}H_{29}N$
Molecular weight/g mol^{-1}	259.42
Temperature	273 (2) K
Wavelength (MoK$_\alpha$)/Å	0.71073
Crystal system	Orthorhombic
Lattice type	Non-centrosymmetric
Space group	$P2_12_12_1$
Form/habit	Block
Crystal size	0.5 × 0.3 × 0.2 mm^3.
Cell parameters from 25 reflections	$a = 5.656$ (1) Å $b = 9.134$ (2) Å $\alpha, \beta, \gamma = 90°$ $c = 31.001$ (6) Å
V_c/Å^3	1601.7 (5)
Z	4
D_x	1.076 Mg m^{-3}
D_m	Not measured
Data collection	
θ-range for data collection	2.98 to 28.46 degree.
Index ranges	$-4 \leqslant h \leqslant 7$, $-8 \leqslant l \leqslant 11$, $-37 \leqslant l \leqslant 38$
Absorption coefficient	0.061 mm^{-1}
F(000)	576
Reflections collected	7579
No. of independent reflections	3457 [R(int) = 0.052]
No. of observed reflections	1979
Refinement	
Refinement method	Full-matrix least-squares on F^2
Max. shift/esd	0.027
Extinction coefficient	0.0056 (7)
w	$1/[\sigma^2(F_o^2) + (0.0375P)^2]$ where $P = (F_o^2 + F_c^2)/3$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0520$, $WR_2 = 0.0884$
R indices (all data)	$R_1 = 0.1228$, $WR_2 = 0.1062$
Absolute structure parameter	3 (5)
Largest diffraction peak and hole	0.147 and −0.188 e Å^{-3}

3. Results and discussion

3.1. *Molecular conformation*

The final positions and thermal parameters of the non-hydrogen atoms are given in tables 2 and 3, respectively. The molecular structure of $3d_1$CC is presented in figure 1 which show the atomic numbering scheme. Displacement

Table 2. Atomic coordinates (×10^{-4}) and equivalent isotropic displacement parameters (×10^{-3}) of the non-hydrogen atoms with e.s.d.s in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
N1	−8289 (2)	5178 (1)	−134 (0)	48 (1)
C1	−6558 (2)	5148 (2)	58 (0)	34 (1)
C2	−4420 (2)	5094 (2)	326 (0)	31 (1)
C3	−4241 (2)	3620 (1)	553 (1)	35 (1)
C4	−4436 (2)	6354 (2)	650 (1)	32 (1)
C5	−2297 (2)	6271 (2)	950 (1)	33 (1)
C6	−2107 (2)	3575 (2)	854 (1)	33 (1)
C7	−2146 (2)	4807 (2)	1189 (0)	25 (1)
C8	−51 (2)	4720 (2)	1507 (0)	25 (1)
C9	−23 (2)	3290 (2)	1763 (1)	29 (1)
C10	−27 (2)	6007 (2)	1824 (1)	31 (1)
C11	2007 (2)	5927 (2)	2141 (0)	31 (1)
C12	2020 (2)	3220 (2)	2084 (0)	31 (1)
C13	2026 (2)	4504 (2)	2399 (0)	30 (0)
C14	4086 (2)	4442 (2)	2704 (0)	31 (1)
C15	3985 (2)	4354 (2)	3126 (0)	31 (1)
C16	6063 (2)	4253 (2)	3426 (0)	32 (1)
C17	5989 (2)	5299 (2)	3803 (0)	34 (1)
C18	8073 (2)	5103 (2)	4107 (1)	39 (1)

Table 3. Anisotropic displacement parameters U_{ij}(×10^{-3}) for non-hydrogen atoms with e.s.d.s in parentheses. The anisotropic displacement factor exponent takes the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	48 (1)	52 (1)	43 (1)	1 (1)	−11 (1)	2 (1)
C1	40 (1)	34 (1)	26 (1)	3 (1)	−1 (1)	1 (1)
C2	30 (1)	38 (1)	25 (1)	3 (1)	1 (1)	−2 (1)
C3	38 (1)	32 (1)	37 (1)	−6 (1)	−10 (1)	4 (1)
C4	34 (1)	30 (1)	32 (1)	2 (1)	−6 (1)	1 (1)
C5	35 (1)	28 (1)	35 (1)	1 (1)	−4 (1)	−2 (1)
C6	35 (1)	27 (1)	37 (1)	−25 (1)	−7 (1)	5 (1)
C7	25 (1)	25 (1)	25 (1)	−1 (1)	2 (1)	0 (1)
C8	24 (1)	27 (1)	26 (1)	2 (1)	0 (1)	−1 (1)
C9	32 (1)	27 (1)	30 (1)	−1 (1)	−4 (1)	−1 (1)
C10	31 (1)	27 (1)	37 (1)	−2 (1)	−4 (1)	1 (1)
C11	32 (1)	28 (1)	32 (1)	−5 (1)	−4 (1)	−1 (1)
C12	36 (1)	27 (1)	29 (1)	2 (1)	−1 (1)	0 (1)
C13	25 (1)	36 (1)	28 (1)	−1 (1)	1 (1)	0 (1)
C14	24 (1)	38 (1)	32 (1)	−1 (1)	1 (1)	−3 (1)
C15	27 (1)	34 (1)	32 (1)	−1 (1)	2 (1)	0 (1)
C16	32 (1)	36 (1)	27 (1)	−3 (1)	0 (1)	2 (1)
C17	35 (1)	39 (1)	28 (1)	0 (1)	1 (1)	0 (1)
C18	39 (1)	42 (1)	35 (1)	−2 (1)	−7 (1)	−4 (1)

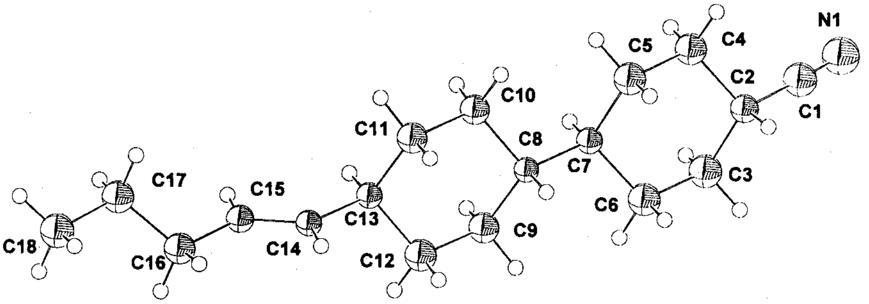

Figure 1. Perspective drawing of $3d_1CC$ showing the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms have an arbitrary radius.

ellipsoids are shown at the 30% probability level and H atoms have an arbitrary radius. Bond lengths and bond angles are consistent with our previous observations and show expected values [1–3]. These are listed in table 4. There is sp^3 hybridization of C_2 and the alkenyl chain is in the all-*trans*-conformation. All the calculations were done using PARST [11].

The compound can be considered in three parts, namely the alkenyl chain, the central core and the cyano group. The puckering parameters of the six-membered rings calculated using the method of Cremer and Pople [12] appear in table 5. For a six-membered ring, there are three puckering degrees of freedom represented by a spherical polar set (Q, θ, ϕ), where Q is the total puckering amplitude and θ is an angle $(0 \leqslant \theta \leqslant \pi)$ such that $q_2 = Q \sin \theta$ and $q_3 = Q \cos \theta$. Here, we have found that the polar positions $(\theta \cong 180°)$ correspond to a chair conformation with $q_2 = 0$ and $q_3 = -Q$. Ring A is defined by the atoms C_2 to C_7 and ring B is defined by the atoms C_8 to C_{13}. The substituents are in a *trans*-conformation with respect to the double bond. The normals to the least-squares mean planes through the alkenyl chain and the attached cyclohexyl ring make the dihedral angle of 34.06 (12)°.

Table 4. Bond distances (Å) and angles (°) with e.s.d.s in parentheses.

Bond distance		Angle	
N1–C1	1.146 (1)	N1–C1–C2	176.76 (4)
C1–C2	1.468 (1)	C1–C2–C4	109.99 (2)
C2–C3	1.523 (2)	C1–C2–C3	110.25 (3)
C2–C4	1.528 (2)	C3–C2–C4	111.27 (8)
C3–C6	1.526 (1)	C2–C3–C6	111.04 (2)
C4–C5	1.528 (1)	C2–C4–C5	110.99 (2)
C5–C7	1.531 (2)	C4–C5–C7	112.46 (2)
C6–C7	1.531 (2)	C3–C6–C7	112.55 (2)
C7–C8	1.543 (1)	C5–C7–C6	108.33 (8)
C8–C9	1.528 (2)	C6–C7–C8	112.60 (2)
C8–C10	1.532 (2)	C5–C7–C8	113.38 (2)
C9–C12	1.526 (1)	C7–C8–C10	112.16 (2)
C10–C11	1.514 (1)	C7–C8–C9	112.56 (2)
C11–C13	1.526 (2)	C9–C8–C10	108.82 (9)
C12–C13	1.526 (2)	C8–C9–C12	112.47 (2)
C13–C14	1.502 (1)	C8–C10–C11	112.72 (2)
C14–C15	1.312 (3)	C10–C11–C13	112.74 (2)
C15–C16	1.502 (1)	C9–C12–C13	112.75 (2)
C16–C17	1.510 (2)	C11–C13–C12	108.61 (10)
C17–C18	1.520 (1)	C12–C13–C14	112.06 (2)
		C11–C13–C14	111.57 (2)
		C13–C14–C15	126.61 (2)
		C14–C15–C16	125.96 (2)
		C15–C16–C17	114.76 (2)
		C16–C17–C18	112.50 (2)

Table 5. Ring puckering parameters (Å, °) of the cyclohexyl rings with e.s.d.s in parentheses. Ring A is defined by the atoms C_2 to C_7; ring B is defined by the atoms C_8 to C_{13}.

Ring	q_2	q_3	Q	θ
A	0.019 (1)	−0.571 (1)	0.571 (1)	178.11 (1)
B	0.004 (1)	−0.562 (1)	0.562 (1)	179.60 (1)

3.2. *Molecular packing*

The length of the molecule in the crystalline state is 16.1 Å. For the calculation of the best planes of the cyclohexyl rings only the four central carbon atoms were used. The two cyclohexyl rings are nearly coplanar with a dihedral angle of 4.05 (4)°. Ring A is planar to within −2.358 (2) Å and ring B to within −2.787 (2) Å. With respect to the crystal packing, no contacts between the polar cyano groups can be observed. Thus, in the compound $3d_1CC$ no molecular association, such as van der Waals interactions, occur in the crystalline state between the cyano groups.

Figure 2 is a projection along the short crystallographic *a*-axis. The figure clearly depicts that the molecules are packed parallel to the crystallographic *c*-axis The molecules are arranged in a head-to-tail fashion in imbricated rows as shown by the projection along the *b*-axis in figure 3. The best fit line through N_1 to C_{14} shows that the molecule makes an angle of 38° with the *c*-axis. This imbricated mode of packing is commonly found in nematogenic compounds [13].

Table 6. Crystal and molecular data of mesogenic 4-alkenyl bicyclohexylnitrile compounds.

Compound	Space group system	Z	Dihedral angle between the two cyclohexyl rings/°[a]	Selected Intermolecular distance/Å	Length in the crystalline state/Å	Average length in nematic phase/Å
$1d_1CC$	Triclinic $P\bar{1}$	2	80.30	3.4 N_{cyano}-C'_{chain}	13.5	13.8
$1d_3CC$	Monoclinic $P2_1/n$	4	34	3.7 N_{cyano}-C'_{chain}	16.1	30
$3d_1CC$	Orthorhombic $P2_12_12_1$	4	4.05	—	16.1	—

[a] For the calculation of the best planes of the cyclohexyl rings only the four central carbon atoms were used for all the compounds.

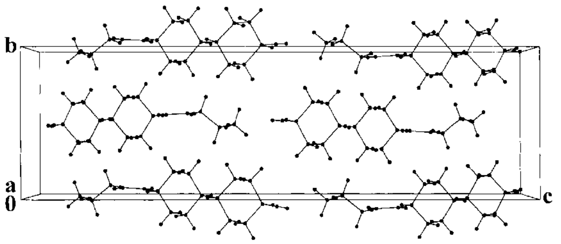

Figure 2. Molecular packing of $3d_1CC$ along [1 0 0].

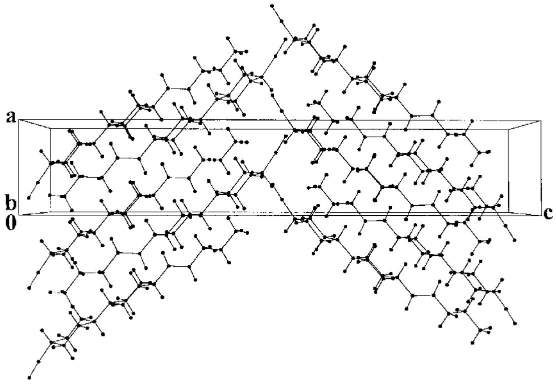

Figure 3. Molecular packing of $3d_1CC$ along [0 1 0].

It is of interest to compare the molecular packing of the two related compounds $1d_3CC$ and $1d_1CC$. All the compounds exhibit nematic behaviour and become isotropic at around 100°C. The compound $3d_1CC$ differs from $1d_3CC$ only with respect to the position of the double bond. $1d_3Cc$ crystallizes in a centrosymmetric monoclinic space group whereas $3d_1CC$ crystallizes in a non-centrosymmetric orthorhombic form. Their elastic constants differ due to the position of the double bond [3]. Thus by changing the position of the double bond, the electro-optical properties of liquid crystals can be affected. Moreover, it has been found that the bend elastic constants of $1d_1CC$ and $3d_1CC$ decrease strongly with increasing chain length [3].

The two cyclohexyl rings adopt chair conformations in all there compounds. The cyclohexyl rings in $1d_1CC$ are approximately perpendicular to each other with a dihedral angle of 80.3° and in $1d_3CC$ it is 34°. In the compound $3d_1CC$ the two rings are nearly coplanar. With respect to crystal packing, intermolecular contacts between polar cyano groups have been observed for $1d_1CC$ and $1d_3CC$ but not $3d_1CC$. Some important crystal data of the three alkenyl compounds are summarized in table 6.

It can be seen that pairs of molecules of $1d_1CC$, related by a centre of symmetry, give rise to a sheet of parallel molecules in the *ac*-plane and these sheets are stacked in an imbricated fashion along the crystallographic *c*-axis. The molecules of the other homologue $1d_3CC$ are related by an inversion centre of symmetry, and lie collinear to each other. They are arranged in layers parallel to the *bc*-plane and the layers are stacked along the *a*-axis.

X-ray diffraction studies in the nematic phase show the presence of dimerization of $1d_3CC$ molecules whereas the measured molecular length is almost equal to the length of a single molecule for $1d_1CC$ [14]. Whether any molecular association occurs at the transition to the nematic phase for $3d_1CC$, is yet to be investigated.

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References

[1] Gupta, S., Nath, A., Paul, S., Schenk, H., and Goubitz, K., 1994, *Mol. Cryst. liq. Cryst.*, **257,** 1.

[2] Gupta, S., Bhattacharyya, K., Sen Gupta, S. P., Paul, S., Kalman, A., and Parkanyi, L., 1999, *Acta Cryst.*, **C55,** 403.

[3] Schadt, M., Buchecker, R., and Muller, K., 1989, *Liq. Cryst.*, **5,** 293.

[4] Enraf-Nonius, 1995. CAD-4 EXPRESS, Version 5.1, Enraf-Nonius, Delft, The Netherlands.

[5] Harms, K., and Wocadlo, S., 1996. XCAD-4, Data Processing Programme, University of Marburg, Germany.

[6] Sheldrick, G. M., 1997, SHELXS-97, A Program for the Solution of Crystal Structures, University of Göttingen, Germany.

[7] Sheldrick, G. M., 1997, SHELXL-97, A Program for the Refinement of Crystal Structures, University of Göttingen, Germany.

[8] Wilson, A. J. C. (editor), 1992, *International Tables for Crystallography*, Vol. C (Dordrecht: Kluwer Academic Publishers).

[9] Flack, H. D., 1983, *Acta Cryst.*, **A39,** 876.

[10] Zsolnai, L., and Huttner, G., 1994, ZORTEP, A program for Molecular Graphics, University of Heidelberg, Germany.

[11] Nardeli, M., 1983, *Comput. Chem.*, **7,** 95.

[12] Cremer, D., and Pople, J. A., 1975, *J. Am. chem. Soc.*, **97,** 1354.

[13] Baumeiser, U., Hartung, H., Gdaniec, M., and Jaskolski, M., 1981, *Mol. Cryst. liq. Cryst.*, **69,** 119.

[14] Nath, A., Choudhury, B., and Paul, S., 1994, *Mol. Cryst. liq. Cryst.*, **265,** 699.