Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Crystal Structure of 4(1″-butenyl) 4″ (cyano)1,1″ bicyclohexane

Sakuntala Gupta [a] , S. P. Sen GUPTA [a] , R. A. Palmer [b] , B. S. Potter [b] & M. Schadt [c]

[a] Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India

[b] Department of Crystallography, Birkbeck College, London, UK

[c] ROLIC Research Ltd., Allschwil, Switzerland

Version of record first published: 18 Oct 2010

To cite this article: Sakuntala Gupta, S. P. Sen GUPTA, R. A. Palmer, B. S. Potter & M. Schadt (2002): Crystal Structure of 4(1″-butenyl) 4″ (cyano)1,1″ bicyclohexane, Molecular Crystals and Liquid Crystals, 378:1, 193-202

To link to this article: http://dx.doi.org/10.1080/713738582

Mol. Cryst. Liq. Cryst., Vol. 378, pp. 193-202

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090156

Crystal Structure of 4(1″-butenyl) 4′ (cyano)1,1′ bicyclohexane

SAKUNTALA GUPTA and S. P. SEN GUPTA

Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India

R. A. PALMER and B. S. POTTER

Department of Crystallography, Birkbeck College, London, UK

M. SCHADT

ROLIC Research Ltd., Allschwil, Switzerland

The crystal and molecular structure of the nematogenic compound 4(1″-butenyl) 4′(cyano)1,1′ bicyclohexane, $C_{17}H_{27}N$, has been determined from X-ray diffraction analysis at 273 K. The compound crystallizes in the form of a centrosymmetric monoclinic system with space group $P2_1/c$, a = 6.4040 (1) Å, b = 20.4180(1) Å, c = 22.9570(1) Å, $\beta = 94.9570(1)^\circ$, and z = 8. Two independent molecules in the crystal have slightly different conformations, but the geometric parameters are normal. The molecular packing is nematic-like.

Keywords: crystal structure, packing, nematogen

INTRODUCTION

As part of our study of the crystal structures of the homologous series of mesogenic cyanoalkenyl compounds, we have solved the crystal structure of the mesogenic compound 4(1″-butenyl) 4′ (cyano)1,1′ bicyclohexane ($0d_3$CC). The position of the double bond at the alkenyl chain markedly affects the structure of the compounds in this series. The crystal structures of $1d_3$CC and $1d_1$CC were determined by us and reported elsewhere [1,2]. The structure of the other homologue $3d_1$CC has been

Received 3 January 2001; accepted 28 November 2001.
Sakuntala Gupta is thankful to CSIR, New Delhi, India, for financial assistance in Scientists' Pool Scheme.
Address correspondance to Sakuntala Gupta, Department of Materials Science, I.A.C.S. Jadavpur, Calcutta - 700 032, India. Email: mssg@mahendra.iacs.res.in

communicated [3]. The compound $0d_3CC$ melts into the nematic state at 50.7°C and into the isotropic phase at 79.8°C [4].

EXPERIMENTAL

Crystal Data

The title compound, $0d_3CC$, was described by Schadt et al. [4]. The crystals of the compound were obtained from a solution in acetone by slow evaporation at 296 (2) K. A crystal of approximate size $0.5 \times 0.2 \times 0.1$ mm^3 was mounted on a CAD-4 EXPRESS equipped with a graphite monochromator and a MoK_α X-ray source ($\lambda = 0.71073$ Å) [5]. The cell dimensions were obtained at 273(2) K and refined by a least-squares fit of 25 reflections ($38° \leq \theta \geq 45°$). A summary of the experimental details is included in Table 1. Data reduction was performed with the program XCAD-4 [6].

STRUCTURE DETERMINATION AND REFINEMENT

The unit cell of the compound $0d_3CC$ studied contains two independent molecules in an asymmetric unit. The structure was solved by SHELXS-97 [7]. The structure was refined by full matrix least-squares using SHELXL-97 [8] with all 6797 unique reflections. The hydrogen atoms were generated at chemically acceptable positions, and those positions were not allowed to vary during the refinement. The H atoms were allowed to ride on their parent atom with $U_{iso}(H) = x\ U_{eq}$(parent), where $x = 1.5$ for methyl and $x = 1.2$ for all others. The nonhydrogen atoms were refined anisotropically. Three hundred twenty-six parameters were refined using all unique reflections. An extinction correction is one of those parameters. The extinction coefficient was found to be 0.0015(3). The atomic scattering factors were taken from International Tables for Crystallography [9]. Finally, for 3559 reflections ($I > 2\sigma(I)$) we have obtained an R-value of 0.0516 and $wR = 0.1127$.

RESULTS AND DISCUSSIONS

Molecular Geometry and Conformation

The positional parameters and equivalent temperature factors for nonhydrogen atoms are given in Table 2. Anisotropic parameters (U_{ij}) are listed

TABLE 1 Summary of crystal data of solution and refinement

Crystal data	
Parameter	Value
Molecular formula	C17 H27 N
Molecular weight /g mol^{-1}	245.40
Temperature	273(2) K
Wavelength (MoKα)/Å	0.71073
Crystal system/lattice type	Monoclinic/centrosymmetric
Space group	$P2_1/c$
Cell parameters from	a = 6.4040(1) Å, b = 20.4180(1) Å,
25 reflections	c = 22.95700(10) Å, β = 94.9570(1)°
Vc/Å^3	2990.56(5)
Z	8
Dx	1.090 mg/m^{-3}
Dm	not measured
Data collection	
Parameter	Value
θ-range for data collection	3.35 to 27.48°
Index ranges	$-8 \le h \le 8, -26 \le k \le 26,$ $-29 \le l \le 29$
Absorption coefficient	0.062 mm^{-1}
F(000)	1088
Reflections collected	24867
No. of independent reflections	6797 [R(int) = 0.0712]
No. of observed reflections	3559
Refinement	
Parameter	Value
Refinement method	Full-matrix, least-squares on F^2
Max.shift/esd	0.356
Extinction coefficient	0.0015(3)
W	$1/[\sigma^2(F_o)^2 + (0.0669P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
Final R indices [I > 2 sigma (I)]	$R_1 = 0.0516$, $wR_2 = 0.1127$
R indices (all data)	$R_1 = 0.1288$, $wR_2 = 0.1394$
Largest diffraction peak and hole	0.251 and −0.201 e Å^{-3}

in Table 3. Bond distances and bond angles are given in Table 4. Figure 1 represents the ORTEP [10] diagram of two molecules A and B of the asymmetric unit, with thermal ellipsoids of 30% probability level. H atoms have an arbitrary radius. Table 5 lists the intermolecular hydrogen bonds in the structure.

The conformation and orientation of the terminal butenyl group is different for the two molecules A and B of asymmetric unit. The torsion angles between the butenyl chain and the cyclohexane ring are given in Table 6. The conformations of the chain of molecules A and B (tabulated positions) are exactly reversed. Thus, the chain of the B molecule in a centrosymme-

TABLE 2 Atomic coordinates and U_{eq} of nonhydrogen atoms with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	U_{eq}
N1A	0.67512(10)	−0.06342(3)	0.52931(3)	0.0414(2)
C1A	−0.94041(12)	0.02228(4)	0.92453(4)	0.0425(3)
C2A	−0.77123(11)	−0.01366(4)	0.93006(3)	0.0338(2)
C3A	−0.58286(11)	−0.00442(4)	0.89739(3)	0.0322(2)
C4A	−0.55410(10)	−0.05951(4)	0.85429(3)	0.0266(2)
C5A	−0.35382(11)	−0.05761(3)	0.82305(3)	0.0242(2)
C6A	−0.33789(11)	−0.11800(4)	0.78457(3)	0.0279(2)
C7A	−0.14370(11)	−0.11839(4)	0.75114(3)	0.0298(2)
C8A	−0.12234(10)	−0.05672(3)	0.71410(3)	0.0236(2)
C9A	−0.13891(11)	0.00353(4)	0.75264(3)	0.0278(2)
C10A	−0.33460(11)	0.00382(4)	0.78603(3)	0.0272(2)
C11A	0.07895(10)	−0.05780(3)	0.68211(3)	0.0241(2)
C12A	0.09431(11)	−0.11915(4)	0.64412(3)	0.0304(2)
C13A	0.29263(11)	−0.12121(4)	0.61222(3)	0.0302(2)
C14A	0.31555(11)	−0.05946(4)	0.57539(3)	0.0282(2)
C15A	0.30315(11)	0.00210(4)	0.61289(3)	0.0289(2)
C16A	0.10233(11)	0.00279(4)	0.64413(3)	0.0270(2)
C17A	0.51527(12)	−0.06132(4)	0.54821(3)	0.0302(2)
N1B	−0.72004(10)	−0.34014(4)	0.59929(3)	0.0453(2)
C1B	0.87599(12)	−0.18400(4)	0.20497(4)	0.0426(3)
C2B	0.71321(11)	−0.15425(4)	0.22270(3)	0.0343(2)
C3B	0.53164(11)	−0.18442(4)	0.24892(3)	0.0336(2)
C4B	0.50730(11)	−0.15933(4)	0.31040(3)	0.0282(2)
C5B	0.30672(11)	−0.17881(3)	0.33726(3)	0.0250(2)
C6B	0.29594(11)	−0.14639(4)	0.39672(3)	0.0286(2)
C7B	0.09959(11)	−0.16499(4)	0.42606(3)	0.0294(2)
C8B	0.07491(10)	−0.23912(3)	0.43317(3)	0.0244(2)
C9B	0.08763(11)	−0.27166(4)	0.37347(3)	0.0274(2)
C10B	0.28388(11)	−0.25270(3)	0.34419(3)	0.0276(2)
C11B	−0.12678(10)	−0.25673(3)	0.46156(3)	0.0238(2)
C12B	−0.13136(11)	−0.22605(4)	0.52230(3)	0.0287(2)
C13B	−0.33172(11)	−0.24163(4)	0.55064(3)	0.0306(2)
C14B	−0.36645(11)	−0.31557(4)	0.55429(3)	0.0273(2)
C15B	−0.36436(11)	−0.34700(4)	0.49377(3)	0.0277(2)
C16B	−0.16327(11)	−0.33051(4)	0.46597(3)	0.0279(2)
C17B	−0.56361(12)	−0.32987(4)	0.58006(3)	0.0319(2)

trically related position must have the same conformation as the A molecule. All the calculations were done by using PARST [11].

The dihedral angles between the mean plane butenyl groups and the cyclohexane moieties are found to be 57.17(4)° and 42.79(3)°, respectively, for molecules A and B of asymmetric unit. The puckering parameters of the rings were calculated using the method of Cremer and Pople [12]. For the 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 ($0 \leq \theta \leq \Pi$) such that $q_2 = Q\ Sin\theta$ and $q_3 = Q\ Cos\theta$. Here, for all cyclohexyl rings the polar positions ($\theta \cong 180°$) correspond to a chair conformation with $q_2 = 0$ and $q_3 = -Q$.

TABLE 3 Anisotropic displacement parameters for nonhydrogen atoms with e.s.d.s in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1A	0.0428(4)	0.0449(4)	0.0384(4)	0.0056(3)	0.0146(3)	0.0093(3)
C1A	0.0369(5)	0.0517(5)	0.0395(5)	−0.0115(4)	0.0075(4)	−0.0024(4)
C2A	0.0331(4)	0.0399(5)	0.0293(4)	−0.0038(4)	0.0087(4)	−0.0033(4)
C3A	0.0303(4)	0.0354(5)	0.0318(4)	−0.0015(4)	0.0084(4)	−0.0027(3)
C4A	0.0253(4)	0.0281(4)	0.0267(4)	0.0006(3)	0.0047(3)	−0.0022(3)
C5A	0.0235(4)	0.0259(4)	0.0236(4)	0.0015(3)	0.0032(3)	−0.0005(3)
C6A	0.0284(4)	0.0240(4)	0.0320(4)	0.0024(3)	0.0071(3)	−0.0017(3)
C7A	0.0338(4)	0.0214(4)	0.0357(4)	0.0005(3)	0.0123(4)	0.0008(3)
C8A	0.0204(3)	0.0249(4)	0.0256(4)	0.0000(3)	0.0032(3)	0.0004(3)
C9A	0.0316(4)	0.0221(4)	0.0309(4)	0.0026(3)	0.0093(3)	0.0001(3)
C10A	0.0301(4)	0.0233(4)	0.0291(4)	0.0011(3)	0.0075(3)	0.0017(3)
C11A	0.0242(4)	0.0233(4)	0.0250(4)	−0.0005(3)	0.0028(3)	0.0005(3)
C12A	0.0312(4)	0.0253(4)	0.0359(4)	−0.0033(4)	0.0092(4)	−0.0008(3)
C13A	0.0309(4)	0.0258(4)	0.0348(4)	−0.0051(4)	0.0090(4)	0.0013(3)
C14A	0.0259(4)	0.0357(4)	0.0237(4)	−0.0033(3)	0.0051(3)	0.0014(3)
C15A	0.0321(4)	0.0278(4)	0.0277(4)	0.0016(3)	0.0075(3)	0.0000(3)
C16A	0.0306(4)	0.0253(4)	0.0261(4)	−0.0001(3)	0.0080(3)	0.0019(3)
C17A	0.0375(4)	0.0293(4)	0.0240(4)	0.0007(3)	0.0043(4)	0.0043(4)
N1B	0.0403(4)	0.0543(5)	0.0428(4)	0.0036(4)	0.0131(3)	−0.0024(3)
C1B	0.0427(5)	0.0443(5)	0.0423(5)	0.0052(4)	0.0120(4)	0.0018(4)
C2B	0.0349(4)	0.0365(5)	0.0322(4)	0.0059(4)	0.0071(4)	0.0014(4)
C3B	0.0328(4)	0.0389(5)	0.0298(4)	0.0014(4)	0.0060(4)	−0.0035(4)
C4B	0.0272(4)	0.0287(4)	0.0289(4)	0.0019(3)	0.0036(3)	−0.0013(3)
C5B	0.0216(3)	0.0267(4)	0.0266(4)	0.0020(3)	0.0018(3)	0.0002(3)
C6B	0.0281(4)	0.0252(4)	0.0330(4)	−0.0026(3)	0.0052(3)	−0.0037(3)
C7B	0.0315(4)	0.0268(4)	0.0306(4)	−0.0062(4)	0.0066(3)	−0.0020(3)
C8B	0.0231(4)	0.0246(4)	0.0255(4)	−0.0019(3)	0.0022(3)	0.0013(3)
C9B	0.0306(4)	0.0251(4)	0.0273(4)	−0.0041(3)	0.0070(3)	−0.0030(3)
C10B	0.0290(4)	0.0274(4)	0.0270(4)	−0.0037(3)	0.0062(3)	0.0003(3)
C11B	0.0225(3)	0.0253(4)	0.0236(4)	−0.0024(3)	0.0013(3)	0.0020(3)
C12B	0.0322(4)	0.0273(4)	0.0270(4)	−0.0064(3)	0.0056(3)	−0.0011(3)
C13B	0.0330(4)	0.0315(4)	0.0281(4)	−0.0057(4)	0.0076(3)	0.0000(3)
C14B	0.0258(4)	0.0324(4)	0.0243(4)	0.0009(3)	0.0050(3)	0.0023(3)
C15B	0.0288(4)	0.0268(4)	0.0276(4)	−0.0012(3)	0.0040(3)	−0.0007(3)
C16B	0.0305(4)	0.0265(4)	0.0272(4)	−0.0039(3)	0.0052(3)	−0.0008(3)
C17B	0.0353(4)	0.0343(4)	0.0264(4)	0.0005(4)	0.0044(4)	0.0026(4)

The molecules have approximately coplanar bicyclohexane moieties and almost all-*trans* zigzag alkenyl chains. The dihedral angles between the rings of the bicyclohexane moieties are found to be 1.43(1)° and 4.02(2)° for molecules A and B, respectively. Nevertheless, despite the different conformation the two independent $0d_3CC$ molecules have nearly the same length in the crystal; the intramolecular distances C(1A)... N(1A) and C(1B)... N(1B) are found to be 14.44 (1) Å and 14.58 (2) Å for molecules A and B, respectively. It should be noted that neither of these molecules is stretched to the maximum possible length because the

TABLE 4 Bond lengths (Å) and bond angles (deg) involving nonhydrogen atoms with e.s.d.s in parentheses

Atoms	*Length*	*Atoms*	*Angle*
N1A C17A	1.1467(10)	C1A C2A C3A	125.61(8)
C1A C2A	1.3056(11)	C2A C3A C4A	112.57(6)
C2A C3A	1.4865(10)	C3A C4A C5A	116.24(6)
C3A C4A	1.5197(11)	C4A C5A C6A	110.70(6)
C4A C5A	1.5232(10)	C4A C5A C10A	113.26(6)
C5A C6A	1.5253(10)	C6A C5A C10A	109.22(6)
C5A C10A	1.5259(10)	C7A C6A C5A	113.34(6)
C6A C7A	1.5167(10)	C6A C7A C8A	113.13(6)
C7A C8A	1.5322(10)	C9A C8A C7A	109.09(6)
C8A C9A	1.5242(10)	C9A C8A C11A	113.08(6)
C8A C11A	1.5378(10)	C7A C8A C11A	111.83(6)
C9A C10A	1.5246(10)	C8A C9A C10A	113.36(6)
C11A C16A	1.5284(10)	C9A C10A C5A	112.72(6)
C11A C12A	1.5344(10)	C16A C11A C12A	108.80(6)
C12A C13A	1.5206(10)	C16A C11A C8A	112.85(6)
C13A C14A	1.5321(11)	C12A C11A C8A	112.38(6)
C14A C17A	1.4712(10)	C13A C12A C11A	113.18(6)
C14A C15A	1.5294(11)	C12A C13A C14A	111.52(6)
C15A C16A	1.5257(10)	C17A C14A C15A	110.44(6)
N1B C17B	1.1483(10)	C17A C14A C13A	109.94(6)
C1B C2B	1.3018(11)	C15A C14A C13A	110.71(6)
C2B C3B	1.4883(11)	C16A C15A C14A	111.04(6)
C3B C4B	1.5223(11)	C15A C16A C11A	112.88(6)
C4B C5B	1.5249(10)	N1A C17A C14A	177.09(8)
C5B C6B	1.5239(10)	C1B C2B C3B	127.44(8)
C5B C10B	1.5255(10)	C2B C3B C4B	112.44(6)
C6B C7B	1.5249(10)	C3B C4B C5B	116.38(6)
C7B C8B	1.5320(10)	C6B C5B C4B	110.72(6)
C8B C9B	1.5317(10)	C6B C5B C10B	108.90(6)
C8B C11B	1.5387(10)	C4B C5B C10B	113.07(6)
C9B C10B	1.5254(10)	C5B C6B C7B	112.98(6)
C11B C16B	1.5291(10)	C6B C7B C8B	112.94(6)
C11B C12B	1.5314(10)	C9B C8B C7B	108.61(6)
C12B C13B	1.5215(10)	C9B C8B C11B	112.90(6)
C13B C14B	1.5293(11)	C7B C8B C11B	111.97(6)
C14B C17B	1.4692(11)	C10B C9B C8B	113.18(6)
C14B C15B	1.5317(10)	C9B C10B C5B	112.77(6)
C15B C16B	1.5234(10)	C16B C11B C12B	109.12(6)
		C16B C11B C8B	113.39(6)
		C12B C11B C8B	111.90(6)
		C13B C12B C11B	112.77(6)
		C12B C13B C14B	111.21(6)
		C17B C14B C13B	110.64(6)
		C17B C14B C15B	110.93(6)
		C13B C14B C15B	110.56(6)
		C16B C15B C14B	111.18(6)
		C15B C16B C11B	112.65(6)
		N1B C17B C14B	178.45(9)

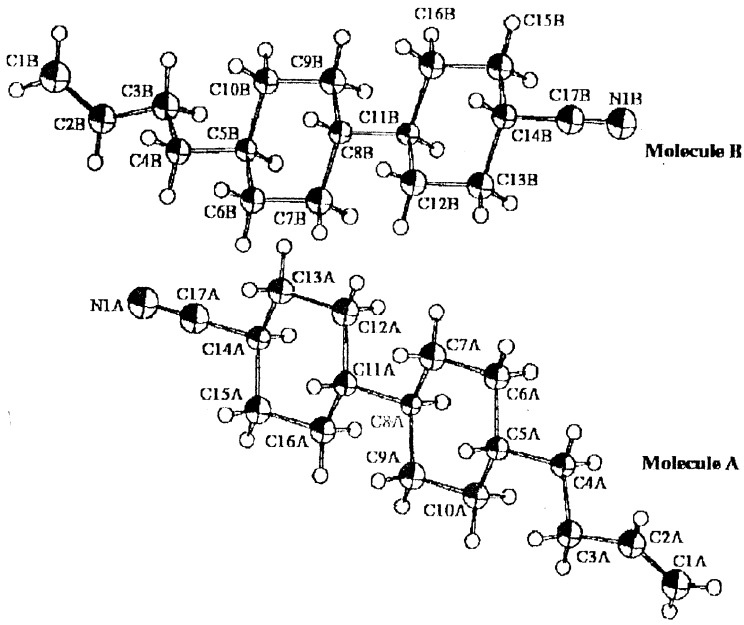

FIGURE 1 ORTEP drawings of the molecules A and B of asymmetric unit with 30% probability thermal ellipsoids.

TABLE 5 Hydrogen-bonding geometry (Å,°)

D–H... A	D–H	D... A	H... A	D–H... A
C15A—H15A—N1A^{i}	0.970 (2)	3.510(3)	2.674 (2)	133.92(14)
C12B—H15B—N1A^{ii}	0.971 (2)	3.554(2)	2.640 (2)	142.03(12)

Symmetry codes: ^{i} $-x+1, -y, -z+1$; ^{ii} $x-1, +y, +z$.
D, Donor; A, Acceptor.

TABLE 6 Torsion angles(°) of the alkenyl chains with e.s.d.s in parenthesis

Chain	Torsion angle/°
Molecule A	
C(1A)-C(2A)-C(3A)-C(4A)	−111.53(9)
C(2A)-C(3A)-C(4A)-C(5A)	−174.33(6)
C(3A)-C(4A)-C(5A)-C(6A)	176.01(6)
C(3A)-C(4A)-C(5A)-C(10A)	60.94(8)
Molecule B	
C(1B)-C(2B)-C(3B)-C(4B)	119.72(9)
C(2B)-C(3B)-C(4B)-C(5B)	170.55(6)
C(3B)-C(4B)-C(5B)-C(6B)	−175.88(6)
C(3B)-C(4B)-C(5B)-C(10B)	61.60(8)

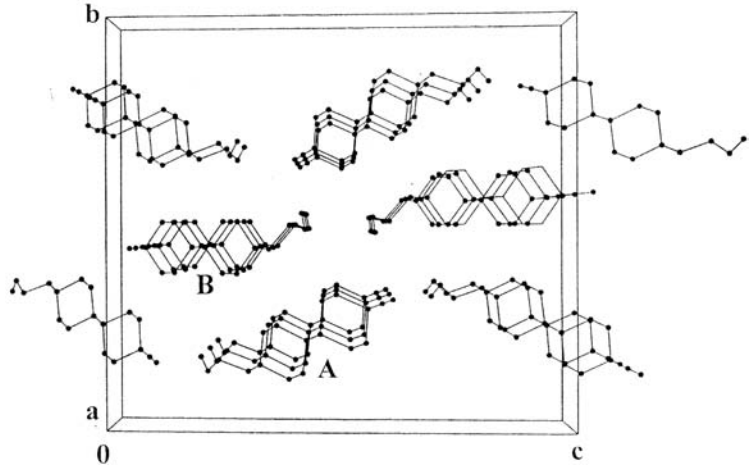

FIGURE 2 Packing of the molecules down the a-axis.

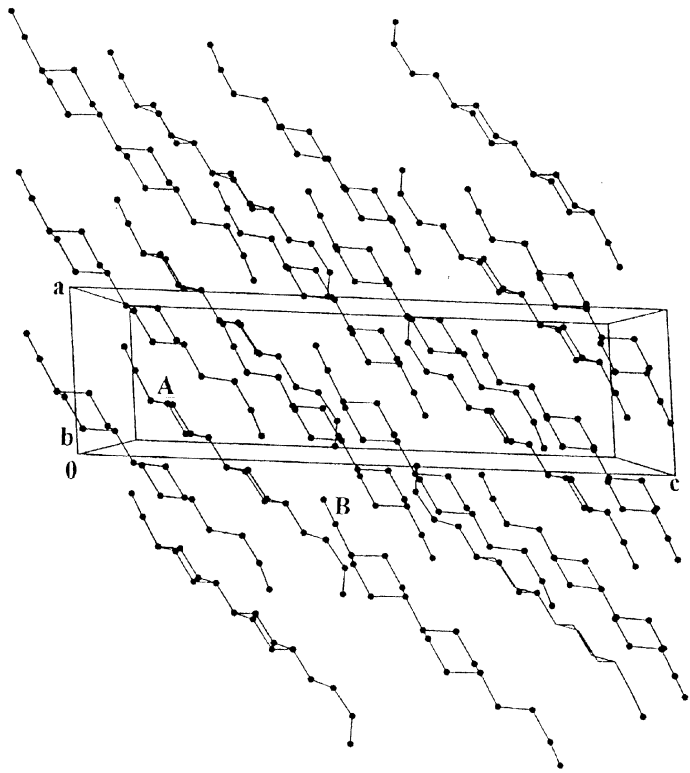

FIGURE 3 Packing of the molecules down the b-axis.

flexible alkenyl chains are inclined to the nearest ring planes, and thereby $0d_3CC$ molecules have a slightly curved shape.

Molecular Packing and Nematic Phase

Figures 2, 3, and 4 show the packing of molecules in the unit cell looking down the a, b, and c axes, respectively. The packing of the molecules indicates strong imbrication down the two directions, as can be seen from Figures 3 and 4. The results are consistent with the necessary requirements for formation of a nematic liquid crystal [13]. The long axes of the molecules A and B are bound into dimers through well-defined hydrogen bonds, as shown in Figure 3, and the associated length was found to be 21.43 Å. As

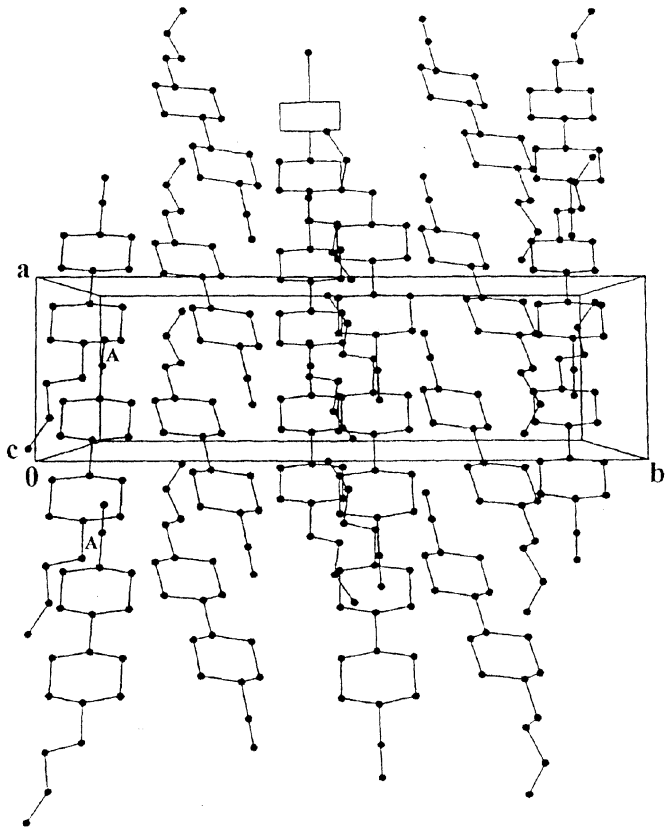

FIGURE 4 Packing of the molecules down the c-axis.

this type of head-to-head overlapping of the molecules becomes stronger in the solid state, the nematic phase is preferred when the compound melts into the mesomorphic phase [13]. The head-to-tail association of the A molecules is parallel to the a-axis (Figure 4). This associated length from C(1) to N(1)′ is found to be 23.7 Å.

With respect to the packing, no contacts between the polar cyano groups can be observed. The best fitted line through N1 to C4 shows that the molecule A makes an angle of 51.26° with the long c-axis. For the B molecule, the respective angle was found to be 58.07°.

REFERENCES

[1] S. Gupta, A. Nath, S. Paul, H. Schenk, and K. Goubitz, *Mol. Cryst. Liq. Cryst.*, **257**, 1–8 (1994).
[2] S. Gupta, K. Bhattacharyya, S. P. Sen Gupta, S. Paul, A. Kalman, and L. Parkanyi, *Acta Cryst.*, **C55**, 403–405 (1999).
[3] S. Gupta, R. A. Palmer, M. Schadt, and S. P. Sen Gupta, Accepted for publication, *Liquid Crystals*, 28, 1309–1313 (2001).
[4] M. Schadt, R. Buchecker, and K. Muller, *Liq. Cryst.*, **5**, 293–312 (1989).
[5] Enraf-Nonius, *CAD-4 EXPRESS. Version 5.1* (Enraf-Nonius, Delft, The Netherlands, 1995).
[6] K. Harms and S. Wocadlo, *XCAD-4. Data Processing Program* (University of Marburg, Germany, 1996).
[7] G. M. Sheldrick, *SHELXS-97. A Program for the Solution of Crystal Structures* (University of Göttingen, Germany, 1997).
[8] G. M. Sheldrick, *SHELXL-97. A Program for the Refinement of Crystal Structures* (University of Göttingen, Germany, 1997).
[9] A. J. C. Wilson, (ed.), *International Tables for Crystallography*, **Vol. C** (Dordrecht: Kluwer Academic Publishers, 1992).
[10] L. Zsolnai and G. Huttner, *ZORTEP. A program for Molecular Graphics* (University of Heidelberg, Germany, 1994).
[11] M. Nardelli, *Comput. Chem.*, **7**, 95 (1983).
[12] D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354–1358 (1975).
[13] D. M. P. Mingos, ed. *Liquid Crystals I, Structure and Bonding* (Springer, 1999) Vol. 94.