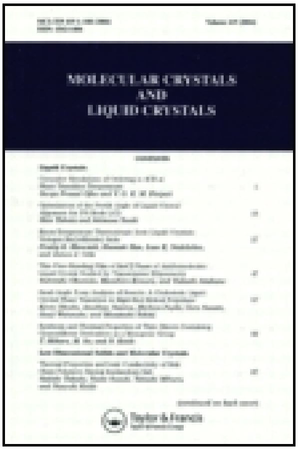

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Arrangement in Mesogenic Compounds with a Terminal Cyano Group

Hassan Allouchi [a], Abdeslam Belaaraj [b], Henry N. C. Wong [c], Huu Tinh Nguyen [d] & Michel Cotrait [e]

[a] Laboratoire de Chimie Physique, Faculté de Pharmacie, 31 Avenue Monge, 37200, Tours, France

[b] Département de Physique, Faculté des Sciences de Meknès, BP 4010-Meknes, Maroc

[c] The Chinese University of Hongkong, Department of Chemistry, Shatin, N. T., Hongkong, China

[d] Centre de Recherche Paul Pascal, Université Bordeauxl, Domaine de Brivazac, 33600, Pessac, France

[e] Laboratoire de Cristallographie, Faculté des sciences, 351 cours de la Libération, 33405, Talence, France

To cite this article: Hassan Allouchi, Abdeslam Belaaraj, Henry N. C. Wong, Huu Tinh Nguyen & Michel Cotrait (1999): Molecular Arrangement in Mesogenic Compounds with a Terminal Cyano Group, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 326:1, 279-290

To link to this article: http://dx.doi.org/10.1080/10587259908025420

Mol. Cryst. Liq. Cryst., Vol. 326, pp. 279–290
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Molecular Arrangement in Mesogenic Compounds with a Terminal Cyano Group

HASSAN ALLOUCHI[a], ABDESLAM BELAARAJ[b], HENRY N. C. WONG[c], HUU TINH NGUYEN[d] and MICHEL COTRAIT[e, *]

[a] *Laboratoire de Chimie Physique, Faculté de Pharmacie, 31 Avenue Monge, 37200 Tours, France;* [b] *Département de Physique, Faculté des Sciences de Meknès, BP 4010-Meknes, Maroc;* [c] *The Chinese University of Hongkong, Department of Chemistry, Shatin, N. T., Hongkong, China;* [d] *Centre de Recherche Paul Pascal, Université Bordeauxl, Domaine de Brivazac, 33600 Pessac, France;* [e] *Laboratoire de Cristallographie, Faculté des sciences, 351 cours de la Libération, 33405 Talence, France*

(Received 18 March 1998; In final form 5 October 1998)

The crystal structures of three mesogenic compounds with a terminal cyano group but with a different polyaromatic central core, showing a nematic and for one of them a cholesteric mesophase, have been solved. The molecular arrangement of two of them is typically nematic while the third one is smectic C-like. All of them involve strong dipolar interactions between their terminal cyano groups with a binding energy ranging -2.7 and -3.8 kcal.mole^{-1} and a dipole moment μ around 3.5 Debye. For the compound with the smectic C-like arrangement the binding energy within the sheet is -17.5 kcal.mole^{-1} while the intersheet energy is as large as -3.9 kcal.mole^{-1}, which is much more than what is observed in mesogenic compounds with a terminal alkyl group.

Keywords: Crystal structures; mesogenic compounds; cyano molecules

INTRODUCTION

During the last decade several crystal structures of nematogenic compounds with a terminal cyano group have been published [1–8]. However, the authors did not emphasize the main contribution played by the highly $C\equiv N$ polar groups on the molecular arrangement in the crystals.

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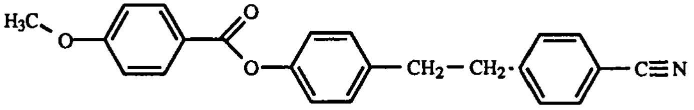
[*] Corresponding author. Tel.: 05 56 84 61 06; Fax: 05 56 84 66 86.

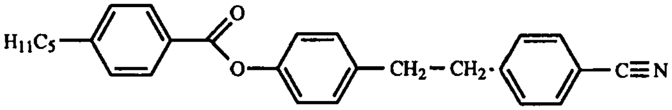
Recently we published the crystal structures of the smectogenic 4-cyanophenyl 4-perfluorohexyl (and heptyl) benzoates, showing the SA_2 mesophase [9–12]. We stressed that the crystal cohesion results from strong dipolar interactions between antiparallel polar $C \equiv N$ groups. In the present paper we analyse the crystal structures of three compounds with a terminal cyano group but with different polyaromatic central cores[1], showing a nematic and for one of them a cholesteric mesophase.

Their chemical formulae are as follows:



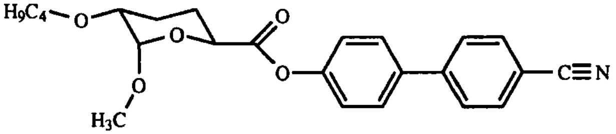
(11)

1



(11)

2



(12)

3

Their mesomorphic sequence is as follows:

$$K \overset{168°C}{- - - - >} N \overset{199°C}{- - - - >} I \qquad (1)$$

$$K \overset{121°C}{- - - - >} N \overset{158°C}{- - - - >} I \qquad (2)$$

$$K \overset{88°C}{- - - - >} (N^*) \overset{(61°C)}{- - - - >} I \qquad (3)$$

The X-ray study will be completed by a theoretical calculation of the binding energy of a molecule within a sheet and between neighbouring sheets for the compound **2** showing a smectic C-like arrangement.

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[1] (1) 1-[4-(4-methoxybenzoyloxy)] phenyl-2-(4-cyanophenyl)ethane, (2) 1-[4-(4-pentylbenzoyloxy)]phenyl-2-(4-cyanophenyl)ethane, (3) 4′,4″-cyanobiphenyl-(methyl 2-O-n-butyl-3,4-di-O-methyl-α-D-gluco-pyranoid)uronate.

EXPERIMENTAL PART

1. Crystal Structures

Colourless prismatic crystals were grown by slow evaporation of ethanol/chloroform solutions. The crystal data are gathered in Table I. The unit cell parameters were obtained by a least-square fit of the setting angles of 25 reflections with Θ between 25 and 42°.

The diffracted intensities were collected with a CAD-4 Enraf-Nonius diffractometer equipped with a graphite monochromator for Θmax = 60°, for compounds **1** and **2** and only 50° for compound 3 and for the CuKα radiation, using the ω-2Θ mode. Three standard reflections were used to monitor the data collection and detect any decrease of the intensities; nevertheless the absorption correction was made using the Ψ scan technique [13]; 3458, 2874 and 1305 reflections were measured respectively for compounds **1**, **2** and **3**, out of which 2937, 2811 and 818 were considered as observed ($I > 2\sigma(I)$).

The crystal structures were solved thanks to SHELXS86 program [14] and refined anisotropically for the C, N and O atoms using constraints on few

TABLE I Crystal data

Compound	**1**	**2**	**3**
Chemical formula	$C_{23}H_{19}NO_3$	$C_{27}H_{27}NO_2$	$C_{24}H_{27}NO_5$
Molecular weight (g. mol^{-1})	357.4	397.5	409.5
Crystal system	triclinic	triclinic	monoclinic
Space group	P1	P$\bar{1}$	P2$_1$
N_b of mol. per unit cell (Z)	2	2	2
a(Å)	8.057(5)	8.213(5)	14.121(5)
b(Å)	9.367(5)	9.890(5)	5.136(3)
c(Å)	13.226(5)	15.476(5)	16.581(4)
α (°)	80.70(1)	107.71(2)	90.000
β (°)	73.44(1)	102.89(2)	110.29(3)
γ (°)	84.75(1)	74.42(2)	90.000
V (Å^3)	943.1	1139.7	1127.9
Density ρ (g.cm^{-3})	1.26	1.16	1.21
Radiation	CuKα	CuKα	CuKα
Wavelength (Å)	1.5418	1.5418	1.5418
Absorption μ (mm^{-1})	0.68	0.57	0.69
h_{min}, h_{max}	0, 9	− 8, 8	− 14,14
k_{min}, k_{max}	− 10, 10	− 9, 9	0,6
l_{min}, l_{max}	− 15, 15	− 15, 15	0,16
Θmax (°)	60	60	50
Measured reflections	3458	2874	1305
Observed reflections	2937	2811	818
Criterium for observed	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R	0.083	0.093	0.099
wR	0.127	0.123	0.117
S	1.06	1.20	1.29

bond lengths, with the SHELXL93 program [15] and with the hydrogen atoms located in their theoretical positions. The final reliability factors were equal to 0.083, 0.093 and 0.099 respectively for compounds **1**, **2** and **3**. The goodness of fit was respectively equal to 1.06, 1.20 and 1.29 for **1**, **2** and **3**. Scattering factors were taken from the International Tables for Crystallography [16].

2. Theoretical Calculations

The partial punctual electronic charges were calculated with the MOPAC 6.0 package, using the MNDO method. The calculations were performed on SGI Indy R4400 Silicon Graphics station, using molecular mechanics with the CVFF (Consistent Force Field) method [17].

The starting conformation was that found in the crystal structure. As we had already observed, preliminary attempts showed that gradient conjugate minimization methods led to large distorsion of the crystalline conformation for an isolated molecule. In the present case where it is essential to preserve the crystalline conformation, the best minimization method is the steepest descent (SD). This procedure was performed without any distance cutoff[2] (the electrostatic interactions are significant even at a large distance) until the energy variation was less than 0.02 kcal/cycle (3000 cycles): the root mean square was less than 0.3 Å at the end of the calculation. The intersheet energy was evaluated by taking into account three sheets with a limited number[3] of molecules per sheet, and by calculating the binding energy between the medium sheet on one side and the lower and upper sheets on the other side.

RESULTS AND DISCUSSION

1. Crystal Structures

The fractional *x*, *y*, *z* coordinates and the equivalent U_{eq} thermal motion factors are listed in Tables II, III and IV respectively for the compounds **1**, **2** and **3**. The U_{eq} values for the carbons of the alkyl or alkoxy chains are quite high; the bond lengths agree quite well with the literature. The molecular

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[2] the cutoff distance is the interatomic distance above which the calculations are no more performed.

[3] the rigorous evaluation of the intersheet energy should involve a much greater number of molecules in every sheet to limit the effects of series endings. Our calculations already involve a great number of molecules, a very large number of interacting pairs and a long calculation time because of the minimization of the optimal conformation of all molecules.

TABLE II Atomic coordinates, equivalent U_{eq} factors and s.o.f. factor for compound **1**

	x/a	y/b	z/c	U_{eq}	s.o.f
C1	−0.7627 (10)	1.1150 (8)	−0.4000 (5)	0.063 (2)	1.0
C2	−0.5924 (11)	1.1560 (11)	−0.4326 (7)	0.091 (3)	1.0
C3	−0.4708 (13)	1.0887 (13)	−0.3811 (8)	0.136 (6)	1.0
C4	−0.5220 (13)	0.9768 (14)	−0.2964 (8)	0.152 (6)	1.0
C5	−0.6900 (15)	0.9401 (14)	−0.2630 (8)	0.113 (5)	1.0
C6	−0.8099 (13)	1.0048 (11)	−0.3144 (7)	0.087 (3)	1.0
C7	−0.4193 (26)	1.0054 (12)	−0.2090 (16)	0.092 (6)	0.5
C7′	−0.3890 (19)	0.8694 (14)	−0.2538 (11)	0.070 (3)	0.5
C8	−0.3074 (19)	0.8611 (13)	−0.2107 (10)	0.057 (3)	0.5
C8′	−0.3420 (41)	0.9475 (18)	−0.1742 (24)	0.092 (12)	0.5
C10	−0.2188 (10)	0.8370 (12)	−0.1213 (6)	0.108 (5)	1.0
C11	−0.1186 (9)	0.7085 (9)	−0.1342 (6)	0.076 (2)	1.0
C12	−0.0225 (11)	0.6565 (9)	−0.0647 (6)	0.073 (2)	1.0
C13	−0.0248 (9)	0.7317 (7)	0.0185 (5)	0.056 (2)	1.0
C14	−0.1234 (10)	0.8592 (8)	0.0331 (7)	0.068 (2)	1.0
C15	−0.2193 (11)	0.9133 (10)	−0.0393 (9)	0.096 (4)	1.0
O16	0.0639 (7)	0.6741 (6)	0.0950 (4)	0.0665 (14)	1.0
C17	0.2371 (9)	0.6725 (7)	0.0622 (5)	0.0513 (15)	1.0
O18	0.3177 (9)	0.7051 (9)	−0.0284 (4)	0.088 (2)	1.0
C20	0.3164 (8)	0.6200 (6)	0.1488 (5)	0.051 (15)	1.0
C21	0.4934 (10)	0.5934 (7)	0.1249 (6)	0.060 (2)	1.0
C22	0.5739 (10)	0.5416 (7)	0.2032 (6)	0.065 (2)	1.0
C23	0.4785 (10)	0.5140 (7)	0.3092 (6)	0.062 (2)	1.0
C24	0.3024 (10)	0.5425 (9)	0.3339 (6)	0.067 (2)	1.0
C25	0.2201 (10)	0.5933 (8)	0.2559 (6)	0.060 (2)	1.0
O26	0.5484 (9)	0.4602 (9)	0.3883 (5)	0.088 (2)	1.0
C27	0.7243 (21)	0.4342 (19)	0.3673 (12)	0.117(5)	1.0
C28	−0.8805 (13)	1.1702 (14)	−0.4571 (8)	0.083 (3)	1.0
N29	−0.9827 (16)	1.2165 (14)	−0.5059 (9)	0.123 (4)	1.0
C51	−0.1529 (10)	0.8279 (8)	0.4608 (6)	0.069 (2)	1.0
C52	−0.3047 (13)	0.7628 (9)	0.4850 (7)	0.100 (4)	1.0
C53	−0.4165 (15)	0.7974 (11)	0.4244 (8)	0.114 (4)	1.0
C54	−0.3763 (13)	0.8959 (9)	0.3355 (8)	0.086 (3)	1.0
C55	−0.2235 (14)	0.9701 (12)	0.3132 (8)	0.099 (3)	1.0
C56	−0.1085 (12)	0.9334 (9)	0.3724 (6)	0.073 (2)	1.0
C57	−0.4919 (23)	0.9246 (17)	0.2584 (13)	0.073 (5)	0.5
C57′	−0.4466 (72)	1.0329 (35)	0.2584 (13)	0.359 (56)	0.5
C58	−0.5799 (16)	1.0755 (13)	0.2703 (12)	0.086 (3)	0.5
C58′	−0.5945 (37)	0.9837 (25)	0.2703 (12)	0.169 (13)	0.5
C60	−0.6934 (10)	1.1057 (10)	0.1877 (7)	0.076 (2)	1.0
C61	−0.7885 (12)	1.2294 (13)	0.1920 (7)	0.096 (4)	1.0
C62	−0.8833 (10)	1.2850 (8)	0.1215 (6)	0.068 (2)	1.0
C63	−0.8839 (8)	1.2119 (7)	0.0423 (6)	0.058 (2)	1.0
C64	−0.7899 (10)	1.0841 (9)	0.0312 (8)	0.073 (2)	1.0
C65	−0.6947 (11)	1.0335 (10)	0.1040 (8)	0.086 (3)	1.0
O66	−0.9708 (6)	1.2660 (6)	−0.0353 (4)	0.0604 (13)	1.0
C67	−1.1493 (11)	1.2668 (9)	−0.0031 (6)	0.059 (2)	1.0
O68	−1.2265 (8)	1.2225 (9)	0.0873 (5)	0.089 (2)	1.0
C70	−1.2290 (9)	1.3192 (6)	−0.0909 (5)	0.051 (2)	1.0
C71	−1.4062 (8)	1.3435 (6)	−0.0650 (5)	0.057 (2)	1.0
C72	−1.4905 (9)	1.3950 (7)	−0.1426 (6)	0.063 (2)	1.0
C73	−1.3938 (10)	1.4235 (7)	−0.2471 (5)	0.059 (2)	1.0
C74	−1.2121 (10)	1.3967 (9)	−0.2752 (6)	0.067 (2)	1.0
C75	−1.1323 (9)	1.3437 (7)	−0.1963 (5)	0.060 (2)	1.0
O76	−1.4568 (9)	1.4768 (9)	−0.3325 (5)	0.092 (2)	1.0
C77	−1.6385 (14)	1.5075 (16)	−0.3136 (11)	0.108 (4)	1.0
C78	−0.0240 (13)	0.7685 (11)	0.5168 (7)	0.076 (2)	1.0
N79	0.0663 (18)	0.7217 (20)	0.5608 (9)	0.140 (6)	1.0

TABLE III Atomic coordinates, equivalent U_{eq} factors and s.o.f. occupation factors for compound 2

	x/a	y/b	z/c	U_{eq}	*s.o.f*
C1	– 0.2638 (10)	0.1136 (8)	– 0.1254 (6)	0.079 (3)	1.0
C2	– 0.3703 (9)	0.0723 (8)	– 0.0902 (5)	0.079 (3)	1.0
C3	– 0.5383 (11)	0.0692 (9)	– 0.1347 (6)	0.087 (3)	1.0
C4	– 0.5989 (10)	0.1070 (11)	– 0.2156 (7)	0.091 (3)	1.0
C5	– 0.4831 (13)	0.1482 (12)	– 0.2506 (7)	0.112 (4)	1.0
C6	– 0.3173 (11)	0.1527 (11)	– 0.2071 (6)	0.098 (3)	1.0
C7	– 0.7654 (44)	0.0845 (30)	– 0.2810 (20)	0.068 (9)	0.5
C7′	– 0.7934 (44)	0.1145 (55)	– 0.2457 (23)	0.143 (18)	0.5
C8	– 0.8494 (30)	0.2169 (34)	– 0.3109 (19)	0.090 (8)	0.5
C8′	– 0.8907 (28)	0.2363 (26)	– 0.2701 (17)	0.061 (6)	0.5
C10	– 1.0472 (11)	0.2238 (11)	– 0.3483 (6)	0.081 (3)	1.0
C11	– 1.1067 (9)	0.0975 (10)	– 0.3982 (5)	0.078 (3)	1.0
C12	– 1.2611 (12)	0.1054 (11)	– 0.4532 (6)	0.096 (3)	1.0
C13	– 1.3632 (9)	0.2386 (10)	– 0.4616 (6)	0.079 (3)	1.0
C14	– 1.3067 (11)	0.3623 (10)	– 0.4128 (7)	0.096 (3)	1.0
C15	– 1.1515 (11)	0.3523 (10)	– 0.3579 (6)	0.081 (3)	1.0
O16	– 1.4871 (13)	0.2353 (14)	– 0.5457 (15)	0.328 (15)	1.0
C17	– 1.6433 (22)	0.2637 (20)	– 0.5320 (17)	0.413 (39)	1.0
O18	– 1.6254 (24)	0.2774 (19)	– 0.4597 (17)	0.441 (24)	1.0
C20	– 1.7880 (20)	0.2688 (10)	– 0.5946 (10)	0.112 (5)	1.0
C21	– 1.9395 (24)	0.3038 (9)	– 0.5697 (8)	0.119 (5)	1.0
C22	– 2.0828 (14)	0.3111 (10)	– 0.6334 (10)	0.109 (4)	1.0
C23	– 2.0774 (16)	0.2835 (11)	– 0.7232 (9)	0.107 (4)	1.0
C24	– 1.9211 (18)	0.2468 (11)	– 0.7511 (7)	0.106 (4)	1.0
C25	– 1.7732 (12)	0.2391 (10)	– 0.6857 (11)	0.102 (4)	1.0
C26	– 2.2401 (23)	0.2804 (18)	–0.7872 (13)	0.218 (10)	1.0
C27	– 2.3334 (24)	0.4101 (21)	–0.8090 (13)	0.255 (12)	1.0
C28	– 2.4651 (25)	0.4244 (27)	– 0.8948 (13)	0.292 (19)	1.0
C29	– 2.6173 (23)	0.4128 (27)	– 0.8708 (15)	0.249 (14)	1.0
C30	– 2.7770 (19)	0.4479 (20)	–0.9441 (14)	0.324 (22)	1.0
C31	– 0.0916 (12)	0.1151 (11)	– 0.0806 (7)	0.087 (3)	1.0
N32	0.0493 (12)	0.1100 (12)	– 0.0511 (8)	0.128 (4)	1.0

conformations are presented along with the atom labelling in Figures 1, 2 and 3.

MOLECULAR CONFORMATIONS

1.1. Compound 1

There are two independent molecules A and B in the asymmetric unit, which are antiparallel (their molecular axes make an angle of only 2°). Their full lengths[4] are close to 24.0 Å. Their molecular conformations are entirely defined by three significative[5] torsion angles (°):

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[4] taking into account the bulkiness of the terminal methyl groups.

[5] differing from 180° by less than 10°.

TABLE IV Atomic coordinates, equivalent U_{eq} factors and s.o.f. occupation factors for compound 3

	x/a	*y/b*	*z/c*	U_{eq}	*s.o.f*
C1	− 0.3311 (9)	− 0.1125 (33)	− 0.0006 (10)	0.116 (5)	1.0
C2	− 0.2833 (13)	− 0.2803 (37)	0.0639 (9)	0.209 (15)	1.0
C3	− 0.1810 (12)	− 0.2804 (41)	0.1059 (11)	0.212 (16)	1.0
C4	− 0.1238 (9)	− 0.0994 (35)	0.0811 (9)	0.108 (5)	1.0
C5	− 0.1687 (13)	0.0719 (44)	0.0167 (12)	0.189 (12)	1.0
C6	− 0.2760 (13)	0.0622 (42)	− 0.0259 (12)	0.228 (14)	1.0
O7	0.6566 (8)	− 0.0144 (40)	0.4425 (8)	0.156 (6)	1.0
C8	0.6378 (11)	0.0775 (68)	0.5132 (12)	0.223 (17)	1.0
C10	− 0.0097 (10)	− 0.1009 (30)	0.1244 (8)	0.100 (4)	1.0
C11	0.0394 (10)	− 0.2792 (29)	0.1892 (9)	0.140 (7)	1.0
C12	0.1411 (12)	− 0.2825 (33)	0.2264 (9)	0.126 (6)	1.0
C13	0.2001 (12)	− 0.1095 (39)	0.2031 (10)	0.132 (6)	1.0
C14	0.1549 (10)	0.0671 (40)	0.1370 (9)	0.132 (7)	1.0
C15	0.0517 (10)	0.0720 (34)	0.1014 (9)	0.113 (5)	1.0
O16	0.3045 (8)	− 0.1454 (31)	0.2373 (11)	0.165 (6)	1.0
C17	0.3562 (12)	0.0575 (49)	0.2846 (11)	0.132 (7)	1.0
O18	0.3207 (10)	0.2540 (45)	0.2915 (12)	0.208 (10)	1.0
C20	0.4703 (9)	− 0.0138 (37)	0.3131 (7)	0.092 (5)	1.0
O21	0.5215 (7)	0.2106 (29)	0.3486 (6)	0.113 (3)	1.0
C22	0.6252 (9)	0.1931 (44)	0.3823 (8)	0.107 (5)	1.0
C23	0.6656 (10)	0.1167 (32)	0.3142 (10)	0.115 (5)	1.0
C24	0.6153 (8)	− 0.1326 (38)	0.2659 (10)	0.112 (5)	1.0
C25	0.5000 (10)	− 0.1075 (36)	0.2389 (9)	0.112 (5)	1.0
O26	0.7705 (8)	0.0775 (35)	0.3464 (7)	0.147 (5)	1.0
C27	0.8209 (15)	0.2488 (71)	0.3105 (19)	0.377 (41)	1.0
C28	0.9303 (26)	0.3076 (93)	0.3161 (14)	0.515 (69)	1.0
C29	0.9787 (18)	0.1348 (88)	0.3928 (19)	0.297 (26)	1.0
C30	1.0862 (20)	0.1589 (90)	0.4051 (15)	0.257 (17)	1.0
C31	− 0.4413 (11)	− 0.1081 (45)	− 0.0473 (9)	0.119 (6)	1.0
N32	− 0.5260 (10)	− 0.1179 (51)	− 0.0854 (10)	0.157 (7)	1.0

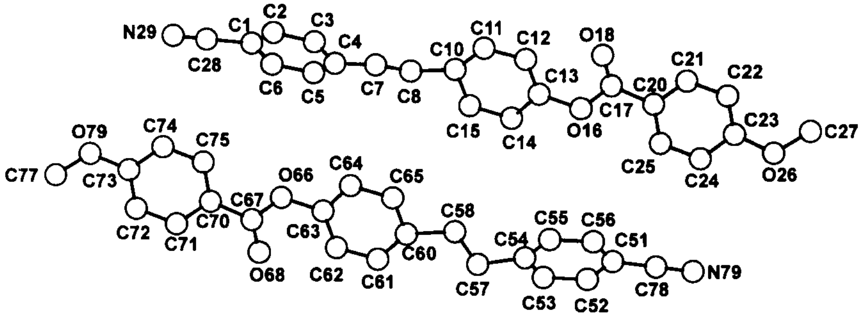

FIGURE 1 Drawing of the molecules A and B of compound 1 along with the atom labelling.

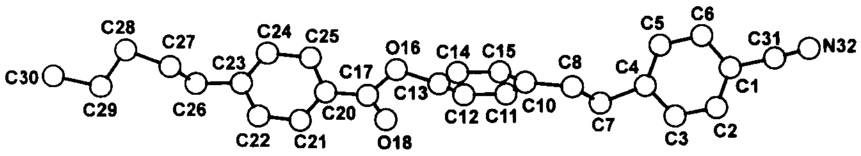

FIGURE 2 Drawing of the molecule of compound 2 along with the atom labelling.

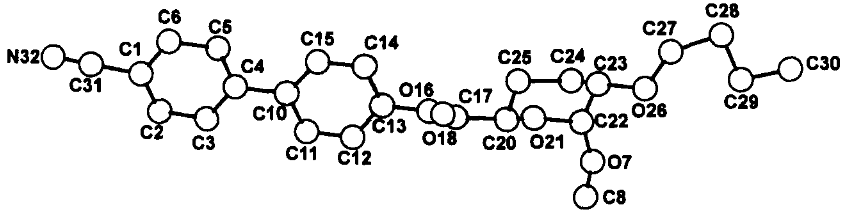

FIGURE 3 Drawing of the molecule of compound **3** along with the atom labelling.

Molecule A		*Molecule B*	
C3-C4-C7-C8	-118(1)	C53-C54-C57-C58	-110(1)
C7-C8-C10-C11	*trans*	C57-C58-C60-C61	*trans*
C12-C13-O16-C17	71(1)	C62-C63-O66-C67	-72(1)

The benzotate groups in both molecules A and B are quite planar. The phenyl groups are named ϕ_{1A} (C1 to C6), ϕ_{2A} (C10 to C15), ϕ_{3A} (C20 to C25), ϕ_{1B} (C51 to C56), ϕ_{2B} (C60 to C65) and ϕ_{3B} (C70 to C75):

$\phi_{2A}/\phi_{1A} = 89(1)$ and $\phi_{3A}/\phi_{2A} = 59(1)°$

$\phi_{2B}/\phi_{1B} = 80(1)$ and $\phi_{3B}/\phi_{2B} = 61(1)°$

The C-CH2-CH2-C(C4-C7-C8-C10 and C54-C57-C58-C60) groups are quasi-planar in both molecules. All these results show that the two independent molecules A and B are very similar and can be related through a pseudoinversion centre $(\bar{1})$. In consequence all molecules are strictly parallel in the crystal network (space group P1). The projection of the structure on the (*xoy*) plane is shown in Figure 4 and is characteristic of a nematic-like arrangement. There are strong dipolar interactions between the terminal C $\equiv$ N groups with the [N79(x, y, z)...N29($1 + x$, y, $1 + z$)] distance of 3.57(2) Å.

1.2. Compound 2

The molecular conformation of the compound **2** is entirely defined by the following significative torsion angles (°):

C3-C4-C7-C8	130(2)	C23-C26-C27-C28	159(2)
C4-C7-C8-C10	146(2)	C26-C27-C28-C29	82(2)
C12-C13-O16-C17	111(2)°	C27-C28-C29-C30	59(2)
C22-C23-C26-C27	91(2)		

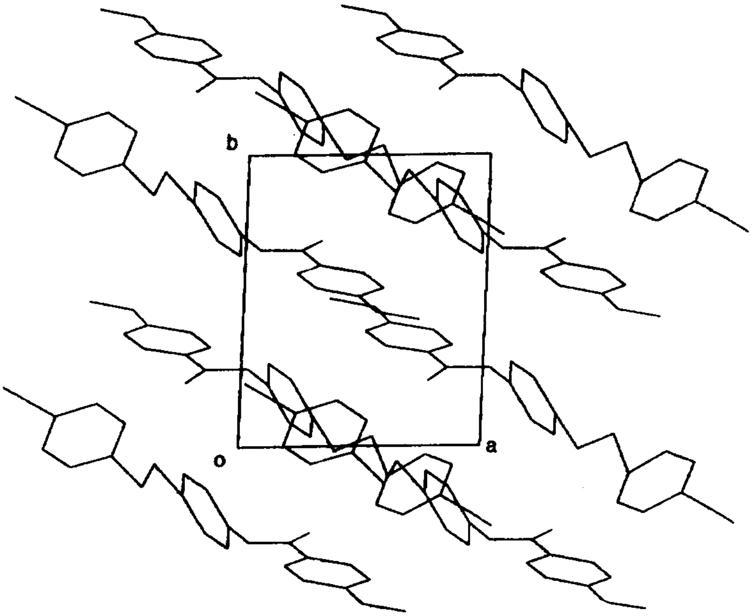

FIGURE 4 Projection of the structure of compound 1 on the (*xoz*) plane.

The terminal pentyl chain is far from being stretched. The phenyl groups are named as for the compound 1: $\phi_2/\phi_1 = 69(2)$ and $\phi_3/\phi_2 = 79(2)°$. The projection of the structure on the (*yoz*) plane is shown in Figure 5. The molecules are arranged in a smectic C-like manner with a sheet thickness of about 14.75 Å. The full length of the molecules is close to 27.7 Å which corresponds to a tilt angle close to 58°. The molecules strongly interact through their antiparallel C ≡ N groups with: Å

$$d[N32(x,y,z)\ldots N32(-x,-y,-z)] = 3.39(2)\text{Å}.$$

1.3. Compound 3

The conformation of the molecule is entirely defined by the following torsion angles (°):

C12-C13-O16-C17	−120(1)	C22-C23-C26-C27	−118(1)
O16-C17-C20-O21	170(1)	C26-C27-C28-C29	−10(1)
O21-C22-O7-C8	−74(1)		

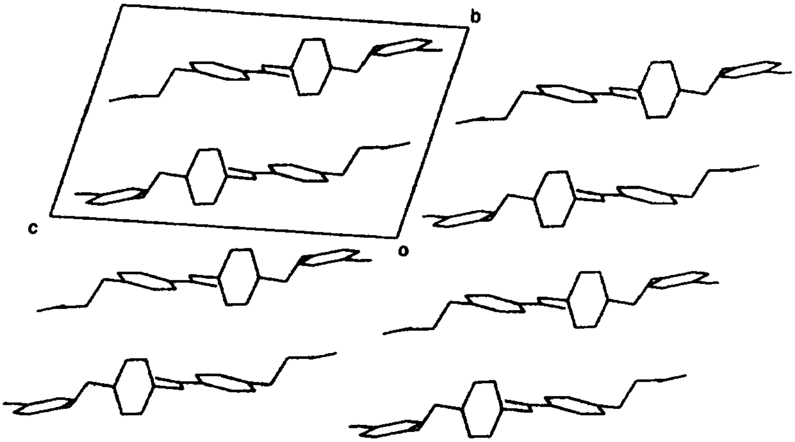

FIGURE 5 Projection of the structure of compound 2 on the (*yoz*) plane.

The pentyl chain is twisted. The ϕ_1 and ϕ_2 rings are rather coplanar, the biphenyl group being roughly planar. The full length of the molecule is close to 24.9 Å. The projection of the structure on the (*xoz*) plane is shown in Figure 6. It can be seen that the molecules are not parallel because of the presence of helicoidal axes, but are arranged in a herring-bone pattern.

Because there are three asymmetric carbon atoms (C20, C22 and C23) this compound gives rise to a homeotropic cholesteric phase. The C $\equiv$ N groups strongly interact:

$$d[N32(x, y, z,) \ldots N32(-1-x, 1/2+y, -z)] \text{ is equal to } 3.70(2)\,\text{Å}$$

2. Theoretical Calculations

For compound **2**, with its smectic C-like arrangement, the binding energy of a given molecule with its six neighbours within a sheet was found equal to −105 kcal, *i.e.*, −17.5 kcal.mole^{-1}, which results from the complete overlap of the molecules. The intersheet energy was found equal to be −3.9 kcal.mole^{-1} (this is quite close to the energy found for a NH...O hydrogen bond in peptides). This energy was found close to −5.0 kcal.mole^{-1} for the ferro and antiferroelectric well-known MHPOBC [18] and C7-Tolane [19] structures where the intersheet energy corresponds to the interaction between their whole hexyl and heptyl terminal chains. But for most of smectogenic molecules which interact only through their

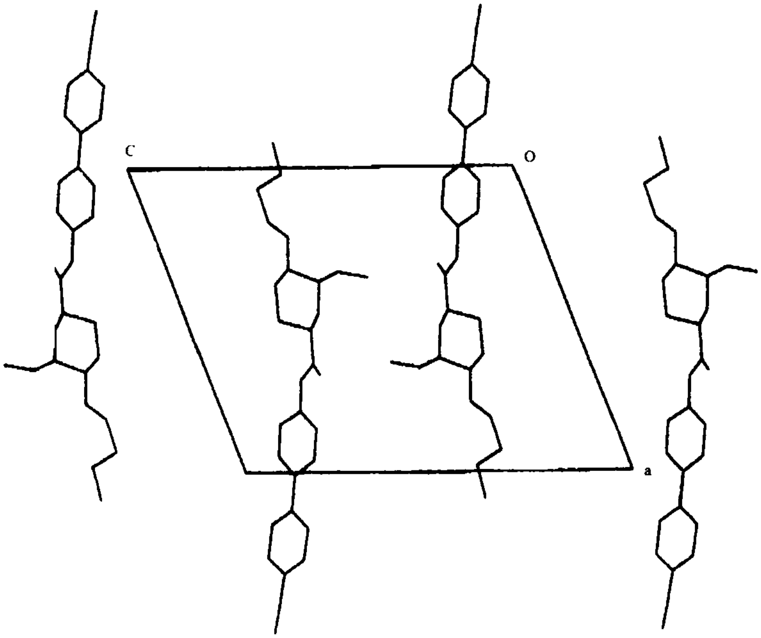

FIGURE 6 Projection of the structure of compound 3 on the (*xoz*) plane.

terminal methyl or ethyl groups this energy is only about $-1.4\,\mathrm{kcal.mole^{-1}}$ [20].

The rather high intersheet energy in smectogenic cyano compounds might reflect a increase of stability of this phase.

Acknowledgement

We thank Dr. Michel Laguerre for performing the theoretical calculations.

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