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# Crystal Structure of a Tetracatenar Mesogen Derived from 3,4-Dialkoxycinnamic Acid

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The crystal structure of a biforked mesogen, exhibiting nematic and smectic phases, derived from 3,4-dialkyloxyphenyl cinnamic acid has been determined by direct methods. The crystal belongs to the $P_{2_1}/c$ space group ($Z = 4$): $a = 42.380(7)$, $b = 9.605(2)$, $c = 18.12(1)$ Å, $\beta = 97.93(2)°$. Least squares refinement leads to $R = 0.091$.

The molecules adopt a zig-zag form and the non-aliphatic central core is almost linear, and 35 Å long. The four alkyloxy chains are stretched (ttt). The mean axis of the alkyloxy chains makes an angle close to 130° with the central core. The molecules make sheets of abour 43 Å thick and are arranged as in a smectic C mesophase. The polyaromatic central core makes an angle close to 70° (tilt angle) with the normal to the sheet and is quasi-parallel to the (xz) plane. The interactions between the sheets are very weak. The structure is compared to those of similar compounds whose structure has recently been published.

*Keywords: mesogenic compound, tetracatenar mesogen, crystal structure*

## INTRODUCTION

Besides rod-like and disc-like mesogenic molecules, several new kinds of molecular designs have recently been shown to be capable of giving thermotropic mesophases.[1,2] The most up-to-date materials belong to the general class of the so-called polycatenar mesogens. These new materials are built-up with classical rod-like core molecules with two or three alkyloxy chains at both extremities. They exhibit a rich variety of mesophases and mesomorphic sequences including lamellar (smectics), columnar, cubic, nematic and several more or less identified bidimensional or tridimensional mesophases.[1,3–6]

The most striking characteristic of these materials is the presence in the same

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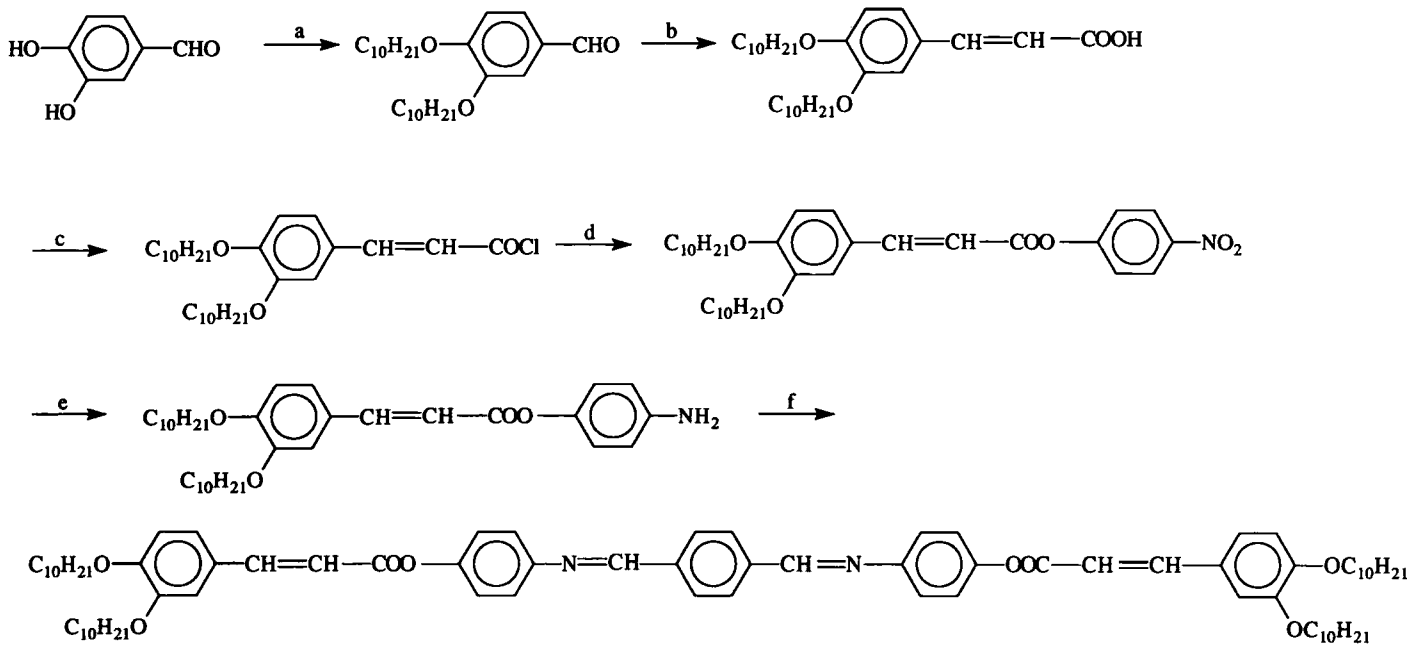



**a** : RBr, $K_2CO_3$, DMF ; **b** : malonic acid, pyridine, piperidine ; oxalyl chloride, toluene ; **d** : p - nitrophenol, pyridine ; **e** : $SnCl_2$, EtOAc ; **f** : terephtaldehyde, benzene, molecular sieves.

SCHEME

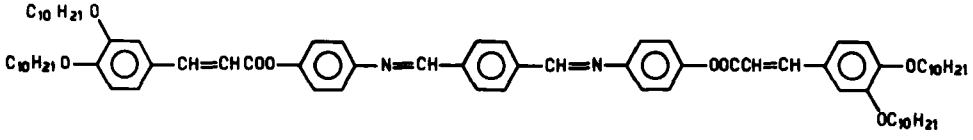
TABLE I

Crystal data

| | |
|---|---|
| $C_{78}H_{108}N_2O_8$ monoclinic | M.W = 1201.7 g mol$^{-1}$ Space group $P_{2_1}/c$ |
| a = 42.38(1) Å | Z = 4 |
| b = 9.60(1) Å | $D_m$ = 1.07 g.cm$^{-3}$ |
| c = 18.12(1) Å | $D_c$ = 1.093 g.cm$^{-3}$ |
| β = 97.93(2)° | λ($CuK_\alpha$) = 1.5418 Å |
| V = 7305 Å$^3$ | μ($CuK_\alpha$) = 5.48 cm$^{-1}$ F(000) = 2616 |

series, and often in the same compound, of lamellar and columnar polymorphism. These substances are attracting more and more interest, especially from a structural point of view. Surprisingly, up to now, no definitive description of the molecular arrangement in the columnar mesophases has been given.[1,4] In fact, most of these mesophases show an hexagonal symmetry, but the cooperative association of these strongly elongated molecules is still puzzling.

This paper aims at describing the structural, conformational and collective molecular organization directly in the crystalline phase. Considering the relatively low crystal mesophase heat of transition, it may be considered that no dramatic intermolecular rearrangement occurs at this transition. So we performed a systematic structural investigation of the crystalline phase of several biforked mesogens derived from (3-(3′-4′-dialkyloxyphenyl)propanoic and cinnamic acid as well as several phasmidic compounds (six aliphatic substituents). Some of these materials exhibit a direct crystal-hexagonal mesophase, and one example was recently published.[7] Now we describe the crystalline arrangement of another biforked mesogen derived from cinnamic acid:




Several physicochemical properties have been published elsewhere[4,6] but the most important mesomorphic characteristic of this compound is the presence of a direct crystal-smectic C transition:

$$K \xrightarrow{144°} S_C \xrightarrow{211°} N \xrightarrow{232°} I$$

In this series, longer derivatives from $C_{12}H_{15}$ to $C_{14}H_{29}$ show an oblique phase $\varnothing_{ob}$.[5] Unfortunately none has been crystallized up to now. The present structure is quite similar to 3-(3′,4′-dialkyloxyphenyl)propanoic acid with $C_{12}H_{25}$ and $C_{13}H_{27}$ alkyl chains, whose crystal structures were recently published.[7,8] The most important feature is the replacement of the $CH_2$—$CH_2$ group by a CH=CH group in the polyaromatic central core.

TABLE II

Atomic coordinates ($\times 10^4$) and equivalent thermal parameters (Å$^2$ $\times$ $10^3$). $U_{eq} = 1/3\ \Sigma_i\ \Sigma_j\ u_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

| | x | y | z | Ueq |
|---|---|---|---|---|
| C1 | 5240 ( 2) | 3289 (10) | 6648 ( 5) | 66 ( 5) |
| C2 | 5057 ( 2) | 3137 (11) | 5959 ( 5) | 71 ( 5) |
| C3 | 4929 ( 2) | 1850 (11) | 5710 ( 5) | 57 ( 5) |
| C4 | 4993 ( 2) | 714 (10) | 6171 ( 5) | 63 ( 5) |
| C5 | 5176 ( 2) | 819 (11) | 6848 ( 5) | 66 ( 5) |
| C6 | 5300 ( 2) | 2140 (11) | 7103 ( 5) | 63 ( 5) |
| C7 | 5473 ( 2) | 2178 (11) | 7865 ( 5) | 71 ( 5) |
| N8 | 5562 ( 2) | 3331 ( 9) | 8150 ( 4) | 71 ( 4) |
| C9 | 4737 ( 2) | 1774 (11) | 4974 ( 5) | 68 ( 5) |
| N10 | 4725 ( 2) | 2702 ( 8) | 4493 ( 4) | 64 ( 4) |
| C11 | 5709 ( 2) | 3417 (11) | 8907 ( 6) | 64 ( 5) |
| C12 | 5943 ( 2) | 4403 (10) | 9113 ( 5) | 71 ( 5) |
| C13 | 6081 ( 2) | 4475 (11) | 9832 ( 5) | 84 ( 5) |
| C14 | 6002 ( 3) | 3534 (12) | 10349 ( 5) | 82 ( 5) |
| C15 | 5758 ( 2) | 2632 (11) | 10153 ( 6) | 94 ( 5) |
| C16 | 5622 ( 2) | 2484 (10) | 9463 ( 6) | 80 ( 5) |
| O17 | 6123 ( 2) | 3626 ( 8) | 11093 ( 4) | 102 ( 4) |
| C18 | 6420 ( 3) | 4070 (13) | 11356 ( 6) | 112 ( 5) |
| O19 | 6595 ( 2) | 4547 ( 8) | 10971 ( 4) | 115 ( 5) |
| C20 | 6452 ( 3) | 3874 (11) | 12194 ( 6) | 111 ( 5) |
| C21 | 4542 ( 2) | 2511 ( 9) | 3816 ( 5) | 54 ( 5) |
| C22 | 4244 ( 2) | 1850 (10) | 3720 ( 5) | 72 ( 5) |
| C23 | 4052 ( 2) | 1722 (10) | 3029 ( 5) | 73 ( 5) |
| C24 | 4158 ( 2) | 2281 (11) | 2421 ( 5) | 66 ( 5) |
| C25 | 4454 ( 2) | 2915 (10) | 2490 ( 5) | 63 ( 5) |
| C26 | 4630 ( 2) | 3044 ( 9) | 3186 ( 5) | 60 ( 5) |
| O27 | 3960 ( 1) | 2263 ( 7) | 1748 ( 4) | 75 ( 4) |
| C28 | 4040 ( 3) | 1460 (11) | 1195 ( 6) | 74 ( 5) |
| O29 | 4279 ( 2) | 777 ( 8) | 1240 ( 4) | 121 ( 5) |
| C30 | 3815 ( 2) | 1532 (10) | 509 ( 6) | 70 ( 5) |
| C40 | 6698 ( 3) | 4426 (11) | 12587 ( 5) | 110 ( 5) |
| C41 | 6792 ( 3) | 4334 (11) | 13401 ( 5) | 84 ( 5) |
| C42 | 7069 ( 3) | 5023 (12) | 13660 ( 6) | 110 ( 5) |
| C43 | 7189 ( 3) | 4987 (11) | 14383 ( 6) | 79 ( 5) |
| C44 | 7029 ( 3) | 4165 (11) | 14878 ( 6) | 78 ( 5) |
| C45 | 6751 ( 2) | 3524 (10) | 14646 ( 5) | 75 ( 5) |
| C46 | 6630 ( 2) | 3582 (10) | 13886 ( 6) | 80 ( 5) |
| O47 | 7466 ( 2) | 5611 ( 8) | 14711 ( 4) | 126 ( 4) |
| O48 | 7178 ( 1) | 4195 ( 7) | 15602 ( 3) | 78 ( 4) |
| C50 | 3856 ( 2) | 924 (10) | -124 ( 5) | 79 ( 5) |
| C51 | 3663 ( 3) | 959 (11) | -840 ( 5) | 73 ( 5) |
| C52 | 3374 ( 2) | 1639 (10) | -1010 ( 6) | 81 ( 5) |
| C53 | 3213 ( 2) | 1675 (10) | -1706 ( 5) | 58 ( 5) |
| C54 | 3325 ( 2) | 898 (10) | -2273 ( 5) | 61 ( 5) |
| C55 | 3605 ( 2) | 219 (10) | -2125 ( 5) | 78 ( 5) |
| C56 | 3771 ( 2) | 233 (10) | -1416 ( 5) | 71 ( 5) |
| O57 | 2925 ( 1) | 2309 ( 7) | -1898 ( 3) | 72 ( 4) |
| O58 | 3137 ( 1) | 998 ( 7) | -2956 ( 3) | 72 ( 4) |
| C61 | 7663 ( 2) | 6141 (12) | 14214 ( 5) | 137 ( 5) |
| C62 | 7973 ( 2) | 6604 (12) | 14686 ( 6) | 161 ( 5) |
| C63 | 8178 ( 3) | 5429 (12) | 15071 ( 7) | 179 ( 5) |
| C64 | 8479 ( 3) | 6162 (13) | 15461 ( 7) | 205 ( 5) |
| C65 | 8717 ( 3) | 5085 (13) | 15818 ( 8) | 213 ( 5) |
| C66 | 9015 ( 3) | 5765 (13) | 16226 ( 8) | 217 ( 5) |
| C67 | 9284 ( 4) | 4767 (14) | 16491 ( 9) | 280 ( 5) |
| C68 | 9574 ( 4) | 5499 (14) | 16925 (10) | 298 ( 5) |
| C69 | 9736 ( 4) | 4089 (16) | 16893 (11) | 386 ( 5) |
| C70 | 10019 ( 4) | 4490 (18) | 17455 ( 9) | 330 ( 5) |
| C71 | 7046 ( 2) | 3314 ( 9) | 16140 ( 4) | 71 ( 4) |
| C72 | 7276 ( 2) | 3414 (10) | 16867 ( 4) | 76 ( 5) |
| C73 | 7609 ( 2) | 2860 (10) | 16785 ( 5) | 92 ( 5) |
| C74 | 7824 ( 2) | 2885 (11) | 17541 ( 5) | 97 ( 5) |
| C75 | 8158 ( 2) | 2371 (11) | 17433 ( 5) | 104 ( 5) |
| C76 | 8382 ( 2) | 2402 (12) | 18170 ( 5) | 124 ( 5) |

TABLE II (*continued*)

| | x | y | z | Ueq |
|---|---|---|---|---|
| C77 | 8718 ( 2) | 1933 (12) | 18059 ( 5) | 124 ( 5) |
| C78 | 8948 ( 2) | 1969 (13) | 18780 ( 6) | 150 ( 5) |
| C79 | 9287 ( 3) | 1564 (15) | 18680 ( 6) | 194 ( 5) |
| C80 | 9507 ( 3) | 1631 (15) | 19420 ( 7) | 226 ( 5) |
| C81 | 2766 ( 2) | 2909 (10) | -1325 ( 4) | 74 ( 4) |
| C82 | 2447 ( 2) | 3460 (10) | -1703 ( 5) | 91 ( 5) |
| C83 | 2228 ( 2) | 2319 (10) | -2076 ( 5) | 100 ( 5) |
| C84 | 1908 ( 2) | 2965 (10) | -2403 ( 5) | 111 ( 5) |
| C85 | 1674 ( 2) | 1900 (11) | -2799 ( 6) | 117 ( 5) |
| C86 | 1355 ( 2) | 2592 (11) | -3123 ( 6) | 133 ( 5) |
| C87 | 1125 ( 2) | 1520 (12) | -3520 ( 6) | 156 ( 5) |
| C88 | 817 ( 3) | 2268 (12) | -3843 ( 7) | 170 ( 5) |
| C89 | 575 ( 3) | 1202 (13) | -4191 ( 8) | 250 ( 5) |
| C90 | 288 ( 3) | 1997 (16) | -4607 ( 8) | 300 ( 5) |
| C91 | 3249 ( 2) | 288 (10) | -3555 ( 4) | 83 ( 5) |
| C92 | 2996 ( 2) | 398 (11) | -4226 ( 4) | 97 ( 5) |
| C93 | 2698 ( 2) | -405 (11) | -4070 ( 5) | 109 ( 5) |
| C94 | 2457 ( 2) | -422 (12) | -4777 ( 5) | 128 ( 5) |
| C95 | 2133 ( 2) | -961 (13) | -4631 ( 5) | 139 ( 5) |
| C96 | 1889 ( 3) | -779 (14) | -5332 ( 5) | 166 ( 5) |
| C97 | 1545 ( 3) | -821 (14) | -5227 ( 6) | 188 ( 5) |
| C98 | 1324 ( 3) | -502 (14) | -5944 ( 6) | 176 ( 5) |
| C99 | 987 ( 3) | -609 (16) | -5783 ( 7) | 265 ( 5) |
| C100 | 773 ( 3) | -128 (15) | -6485 ( 8) | 260 ( 5) |

## EXPERIMENTAL

### Synthesis

The compound was prepared starting with alkylation of 3,4-dihydroxybenzaldehyde. Knoevenagel condensation of the aldehyde with malonic acid, treatment of the cinnamic acid with oxalyl chloride and condensation of the acid chloride with 4-nitrophenol furnished 4-nitrophenyl 3,4-dialkoxycinnamate. Reduction of the nitro group with tin(II) dichloride gave the corresponding amine. Condensation of the amine with the terephthaldehyde afforded the target imine. The synthetic route is outlined in the Scheme and full details of the preparation are given in the experimental section of a previous paper.[5]

### Crystal Data and X-Ray Measurements

Yellow plate crystals were obtained with some difficulty by slow evaporation from toluene solutions. They were fragile, soft and often twinned. The unit-cell parameters were obtained by a least-squares fit of the setting angles of 25 reflections with $\theta$ between 15 and 35°. The crystal data are given in Table I.

The data were collected on a Nonius CAD-4 diffractometer, equipped with a graphite monochromator, for the $CuK_\alpha$ radiation with $\sin\theta/\lambda < 0.50$ ($-41 \leq h \leq 41$, $0 \leq k \leq 9$, $0 \leq 1 \leq 17$) and an $\omega$-$2\theta$ scan; scan range: $(2.0 + 0.15 \tan\theta)°$; detector width: $(2.1 + 1.0 \tan\theta)$ mm; reflections with $\theta < 25°$ were measured twice and averaged; experimental absorption correction: minimum and maximum transmission factors of 0.94 and 0.98, respectively. Three reflections ($-9$ 1 2, $-9$ $-1$ $-2$, 22 0 $-2$) were used as references and monitored every 200 reflections. Of 8082 independent reflections measured, only 2760 were considered as observed [$I > 3\sigma(I)$].

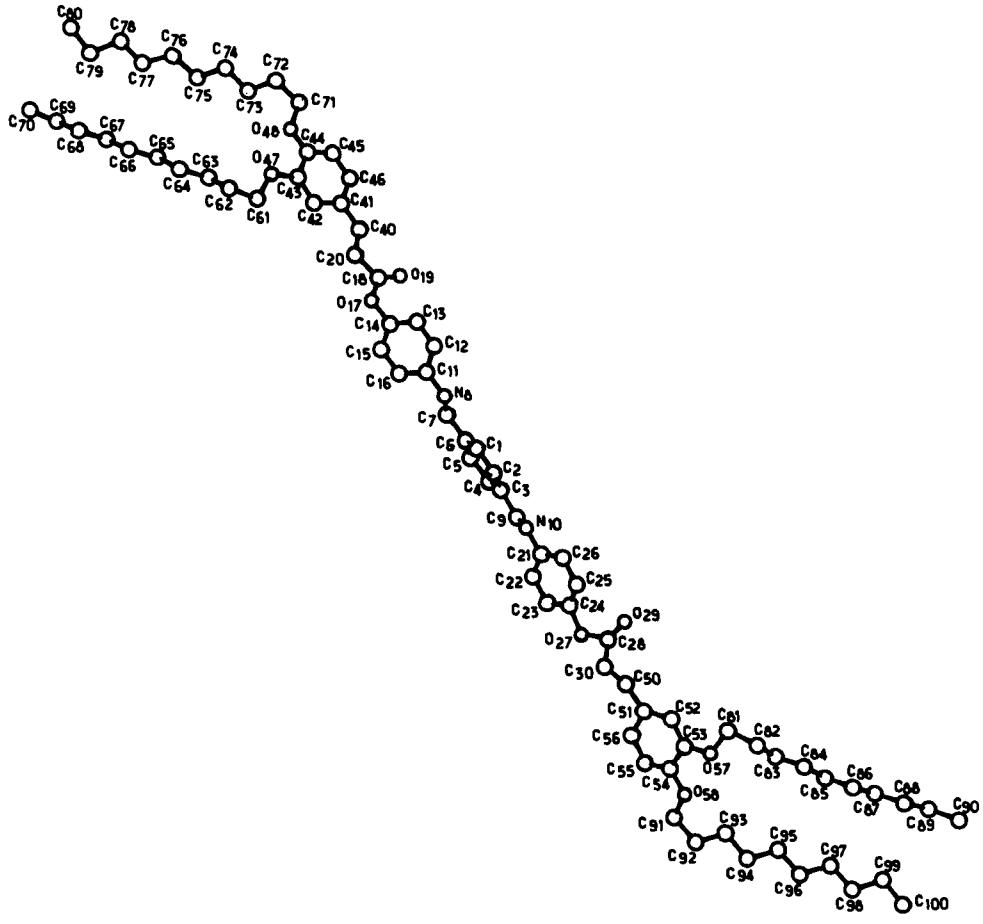



FIGURE 1 Atomic labeling.

### Structure Analysis and Refinement

The structure was solved by direct methods using the Mithril package.[9] An E-map showed the central core of the molecule. The remaining C-atoms of the alkyl chains were located in two subsequent Fourier maps. The structure was refined by block diagonal least-squares, first with isotropic, then anisotropic factors for non-hydrogen atoms, minimizing $w(|F_0| - |F_C|)^2$ where $w = 1/\sigma^2(F_0)$.

Owing to the high thermal motions of most C, N, O atoms, hydrogen atoms were positioned in their theoretical positions[10]; the refinement was then resumed. Diffusion factors for non-hydrogen atoms,[11] or for hydrogens,[12] were used. The final reliability factor was R = 0.091, and the residual electronic density was between $-0.3$ and $0.25e\ Å^{-3}$.

The rather limited number of reflections observed, according to the number (88) of C, N, O atoms to be determined and the high thermal motions of the alkyloxy chains, explains the relatively high R factor. Such relatively high R factors have often been observed for mesogenic crystal structures.[13-16]

TABLE IIIa

Bond lengths (Å) with standard deviations

| | | | | | |
|---|---|---|---|---|---|
| C1 | - C2 | 1.382 (13) | C51 | - C52 | 1.387 (14) |
| C1 | - C6 | 1.380 (14) | C51 | - C56 | 1.386 (14) |
| C2 | - C3 | 1.400 (14) | C52 | - C53 | 1.348 (14) |
| C3 | - C4 | 1.378 (14) | C53 | - C54 | 1.403 (14) |
| C3 | - C9 | 1.465 (13) | C53 | - O57 | 1.365 (11) |
| C4 | - C5 | 1.361 (13) | C54 | - C55 | 1.348 (14) |
| C5 | - C6 | 1.426 (14) | C54 | - O58 | 1.379 (11) |
| C6 | - C7 | 1.471 (13) | C55 | - C56 | 1.378 (14) |
| C7 | - N8 | 1.258 (13) | C61 | - C62 | 1.530 (15) |
| N8 | - C11 | 1.429 (12) | C62 | - C63 | 1.534 (16) |
| C9 | - N10 | 1.242 (12) | C63 | - C64 | 1.539 (18) |
| N10 | - C21 | 1.368 (12) | C64 | - C65 | 1.524 (18) |
| C11 | - C12 | 1.385 (14) | C65 | - C66 | 1.520 (19) |
| C11 | - C16 | 1.435 (14) | C66 | - C67 | 1.518 (20) |
| C12 | - C13 | 1.354 (13) | C67 | - C68 | 1.532 (22) |
| C13 | - C14 | 1.374 (15) | C68 | - C69 | 1.524 (21) |
| C14 | - C15 | 1.361 (15) | C69 | - C70 | 1.511 (25) |
| C14 | - O17 | 1.377 (12) | C71 | - C72 | 1.529 (11) |
| C15 | - C16 | 1.311 (14) | C72 | - C73 | 1.532 (12) |
| O17 | - C18 | 1.350 (16) | C73 | - C74 | 1.538 (12) |
| C18 | - O19 | 1.180 (15) | C74 | - C75 | 1.536 (12) |
| C18 | - C20 | 1.518 (14) | C75 | - C76 | 1.529 (13) |
| C20 | - C40 | 1.292 (15) | C76 | - C77 | 1.532 (13) |
| C21 | - C22 | 1.403 (14) | C77 | - C78 | 1.519 (14) |
| C21 | - C26 | 1.350 (13) | C78 | - C79 | 1.522 (15) |
| C22 | - C23 | 1.402 (13) | C79 | - C80 | 1.525 (17) |
| C23 | - C24 | 1.358 (13) | C81 | - C82 | 1.526 (12) |
| C24 | - C25 | 1.382 (13) | C82 | - C83 | 1.532 (13) |
| C24 | - O27 | 1.382 (11) | C83 | - C84 | 1.534 (13) |
| C25 | - C26 | 1.381 (12) | C84 | - C85 | 1.532 (14) |
| O27 | - C28 | 1.344 (13) | C85 | - C86 | 1.546 (14) |
| C28 | - O29 | 1.199 (13) | C86 | - C87 | 1.529 (15) |
| C28 | - C30 | 1.459 (15) | C87 | - C88 | 1.536 (16) |
| C30 | - C50 | 1.319 (14) | C88 | - C89 | 1.523 (18) |
| C40 | - C41 | 1.476 (13) | C89 | - C90 | 1.540 (20) |
| C41 | - C42 | 1.373 (16) | C91 | - C92 | 1.510 (11) |
| C41 | - C46 | 1.389 (14) | C92 | - C93 | 1.539 (13) |
| C42 | - C43 | 1.338 (15) | C93 | - C94 | 1.523 (13) |
| C43 | - C44 | 1.433 (15) | C94 | - C95 | 1.525 (13) |
| C43 | - O47 | 1.381 (13) | C95 | - C96 | 1.532 (14) |
| C44 | - C45 | 1.343 (14) | C96 | - C97 | 1.495 (16) |
| C44 | - O48 | 1.375 (12) | C97 | - C98 | 1.526 (15) |
| C45 | - C46 | 1.402 (13) | C98 | - C99 | 1.499 (17) |
| C50 | - C51 | 1.435 (14) | C99 | - C100 | 1.529 (19) |

## RESULTS AND DISCUSSION

### Molecular Structure

Atomic parameters (x, y, z and Beq) are given in Table II. The labeling of the atoms is given in Figure 1. As expected, the polyaromatic central core has a significantly smaller thermal motion than those of the alkyloxy chains, particularly for two of them: chain 1 (C(61) to C(70)) and chain 3 (C(81) to C(90)). Bond lengths and bond angles are given in Table III (a and b). They are in good agreement with those observed in similar mesogens,[7,8] except for a few C—C distances and C—C—C angles in the alkyl chains, according to the high thermal motion of those chains, as is often observed in mesogens.[14,17] The molecule adopts a zig-zag form, as can be seen in Figure 2a, already observed for the saturated analogues.[7,8] The

TABLE IIIb

Bond angles (°) with standard deviations

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2 - C1 - C6 | 119.3 ( 9) | C44 - C43 - O47 | 114.7 ( 9) |
| C1 - C2 - C3 | 121.9 ( 9) | C43 - C44 - C45 | 121.7 (10) |
| C2 - C3 - C4 | 117.9 ( 9) | C43 - C44 - O48 | 113.0 ( 9) |
| C2 - C3 - C9 | 118.7 ( 9) | C45 - C44 - O48 | 125.1 ( 9) |
| C4 - C3 - C9 | 123.4 ( 9) | C44 - C45 - C46 | 118.3 ( 9) |
| C3 - C4 - C5 | 121.8 ( 9) | C41 - C46 - C45 | 119.9 ( 9) |
| C4 - C5 - C6 | 119.8 ( 9) | C30 - C50 - C51 | 130.4 ( 9) |
| C1 - C6 - C5 | 119.2 ( 9) | C50 - C51 - C52 | 126.1 ( 9) |
| C1 - C6 - C7 | 124.6 ( 9) | C50 - C51 - C56 | 117.6 ( 9) |
| C5 - C6 - C7 | 116.1 ( 8) | C52 - C51 - C56 | 116.3 ( 9) |
| C6 - C7 - N8 | 119.3 ( 9) | C51 - C52 - C53 | 122.5 ( 9) |
| C7 - N8 - C11 | 120.8 ( 8) | C52 - C53 - C54 | 119.6 ( 9) |
| C3 - C9 - N10 | 124.5 ( 9) | C52 - C53 - O57 | 124.6 ( 9) |
| C9 - N10 - C21 | 119.8 ( 8) | C54 - C53 - O57 | 115.5 ( 8) |
| N8 - C11 - C12 | 120.0 ( 9) | C53 - C54 - C55 | 119.3 ( 9) |
| N8 - C11 - C16 | 121.1 ( 9) | C53 - C54 - O58 | 114.1 ( 8) |
| C12 - C11 - C16 | 118.9 ( 9) | C55 - C54 - O58 | 126.5 ( 9) |
| C11 - C12 - C13 | 119.4 ( 9) | C54 - C55 - C56 | 120.3 ( 9) |
| C12 - C13 - C14 | 120.7 ( 9) | C51 - C56 - C55 | 121.8 ( 9) |
| C13 - C14 - C15 | 119.2 (10) | C61 - C62 - C63 | 115.5 ( 9) |
| C13 - C14 - O17 | 122.2 ( 9) | C62 - C63 - C64 | 104.7 (10) |
| C15 - C14 - O17 | 117.6 ( 9) | C63 - C64 - C65 | 110.0 (10) |
| C14 - C15 - C16 | 122.5 (10) | C64 - C65 - C66 | 111.8 (11) |
| C11 - C16 - C15 | 118.7 ( 9) | C65 - C66 - C67 | 115.0 (12) |
| C14 - O17 - C18 | 124.6 ( 9) | C66 - C67 - C68 | 112.8 (12) |
| O17 - C18 - O19 | 123.0 (11) | C67 - C68 - C69 | 84.7 (12) |
| O17 - C18 - C20 | 105.4 ( 9) | C68 - C69 - C70 | 94.0 (13) |
| O19 - C18 - C20 | 131.5 (11) | C71 - C72 - C73 | 112.4 ( 7) |
| C18 - C20 - C40 | 117.0 (10) | C72 - C73 - C74 | 110.5 ( 7) |
| N10 - C21 - C22 | 124.0 ( 8) | C73 - C74 - C75 | 109.0 ( 7) |
| N10 - C21 - C26 | 121.3 ( 8) | C74 - C75 - C76 | 110.8 ( 8) |
| C22 - C21 - C26 | 114.6 ( 9) | C75 - C76 - C77 | 110.8 ( 8) |
| C21 - C22 - C23 | 123.6 ( 9) | C76 - C77 - C78 | 112.2 ( 8) |
| C22 - C23 - C24 | 118.2 ( 9) | C77 - C78 - C79 | 113.3 ( 9) |
| C23 - C24 - C25 | 119.9 ( 9) | C78 - C79 - C80 | 110.9 (10) |
| C23 - C24 - O27 | 118.8 ( 9) | C81 - C82 - C83 | 113.3 ( 7) |
| C25 - C24 - O27 | 121.1 ( 8) | C82 - C83 - C84 | 109.3 ( 7) |
| C24 - C25 - C26 | 119.5 ( 8) | C83 - C84 - C85 | 113.0 ( 8) |
| C21 - C26 - C25 | 124.1 ( 9) | C84 - C85 - C86 | 111.4 ( 8) |
| C24 - O27 - C28 | 118.8 ( 8) | C85 - C86 - C87 | 110.8 ( 8) |
| O27 - C28 - O29 | 124.0 (10) | C86 - C87 - C88 | 108.6 ( 9) |
| O27 - C28 - C30 | 114.0 ( 9) | C87 - C88 - C89 | 109.4 (10) |
| O29 - C28 - C30 | 122.0 (10) | C88 - C89 - C90 | 108.0 (11) |
| C28 - C30 - C50 | 124.8 ( 9) | C91 - C92 - C93 | 109.1 ( 7) |
| C20 - C40 - C41 | 127.6 (10) | C92 - C93 - C94 | 108.8 ( 8) |
| C40 - C41 - C42 | 114.3 ( 9) | C93 - C94 - C95 | 111.8 ( 8) |
| C40 - C41 - C46 | 125.3 ( 9) | C94 - C95 - C96 | 109.8 ( 9) |
| C42 - C41 - C46 | 120.4 (10) | C95 - C96 - C97 | 116.7 ( 9) |
| C41 - C42 - C43 | 120.9 (10) | C96 - C97 - C98 | 112.5 (10) |
| C42 - C43 - C44 | 118.6 (10) | C97 - C98 - C99 | 108.1 (10) |
| C42 - C43 - O47 | 126.7 (10) | C98 - C99 - C100 | 106.8 (11) |

significant torsion angles, which define the polyaromatic central core, are given in Table IV. All the alkyl chains are extended with C—C—C—C torsion angles moving 180° apart, never by less or more than 10°, and can be considered as almost planar.

The four chains are labeled as follows: chain 1 corresponds to atoms C(61) to C(70), chain 2 to atoms C(71) to C(80), etc. . . .

All O—C—C—C dihedral angles at the beginning of each alkyloxy chain differ from 180°: 67°, −63°, 64° and −65°, respectively for chains 1 to 4. The length of the 1 to 4 aliphatic chains are quite similar: 11.4, 11.3, 11.4, 11.1 Å long, respectively.

TABLE IV

Significant torsion angles (°) with standard deviations

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1) | - | C(6) | - | C(7) | - | C(8) | - 2(1)° |
| C(2) | - | C(3) | - | C(9) | - | C(10 | 14(1)° |
| C(6) | - | C(7) | - | C(8) | - | C(11) | < 2(1)° |
| C(3) | - | C(9) | - | C(10) | - | C(21) | < 2(1)° |
| C(7) | - | N(8) | - | C(11) | - | C(12) | 147(1)° |
| C(9) | - | N(10) | - | C(21) | - | C(22) | 40(1)° |
| C(13) | - | C(14) | - | O(17) | - | C(18) | - 37(1)° |
| C(23) | - | C(24) | - | O(27) | - | C(28) | - 110(1)° |
| C(14) | - | O(17) | - | C(18) | - | C(20) | 156(1)° |
| C(24) | - | O(27) | - | C(28) | - | C(30) | 180(1)° |
| O(17) | - | C(18) | - | C(20) | - | C(40) | 132(1)° |
| O(27) | - | C(28) | - | C(30) | - | C(50) | 172(1)° |
| C(18) | - | C(20) | - | C(40) | - | C(41) | 152(1)° |
| C(28) | - | C(30) | - | C(50) | - | C(51) | - 177(1)° |
| C(20) | - | C(40) | - | C(41) | - | C(42) | - 94(1)° |
| C(30) | - | C(50) | - | C(51) | - | C(52) | - 3(1)° |
| C(43) | - | O(47) | - | C(61) | - | C(62) | -171(2)° |
| C(44) | - | O(48) | - | C(71) | - | C(72) | 175(2)° |
| C(53) | - | O(57) | - | C(81) | - | C(82) | -176(2)° |
| C(54) | - | O(58) | - | C(91) | - | C(92) | 177(2)° |
| C(42) | - | C(43) | - | O(47) | - | C(61) | -10(2)° |
| C(45) | - | C(44) | - | O(48) | - | C(71) | 5(2)° |
| C(52) | - | C(53) | - | O(57) | - | C(81) | -5(2)° |
| C(55) | - | C(54) | - | O(58) | - | C(91) | -4(2)° |
| O(47) | - | C(61) | - | C(62) | - | C(63) | 68(1)° |
| O(48) | - | C(71) | - | C(72) | - | C(73) | - 63(1)° |
| O(57) | - | C(81) | - | C(82) | - | C(83) | 64(1)° |
| O(58) | - | C(91) | - | C(92) | - | C(93) | - 65(1)° |

The projection of the structure along the b axis is shown in Figure 2a. The salient feature is that the mean planes of the contiguous alkyl chains are not parallel, as is observed in the crystal structure of similar compounds.[7,8] The mean planes of chains 1 and 2 make an angle of 75°, while those of chains 3 and 4 make an angle of 56°.

The angle between the central core axis and the orientation of both alkyloxy chains is close to 130°. This core is 35.4 Å long (distance between O(48) and O(58)).

The central $\varphi_0$ cycle defined by atoms C(1) to C(6), its adjacent cycles $\varphi_1$ and $\varphi_1'$ defined by atoms C(11) to C(16) and C(21) to C(26), respectively and the following cycles $\varphi_2$ and $\varphi_2'$ defined by atoms C(41) to C(46) and C(51) to C(56), respectively, characterize the geometry of the polyaromatic central cores. The angles between $\varphi_0$ on one side, and $\varphi_1$ and $\varphi_1'$ on the other side are, respectively, 31° and 51°; the angles between $\varphi_1$ and $\varphi_1'$ with the adjacent cycles $\varphi_2$ and $\varphi_2'$ are, respectively, 14 and 64°. This can be seen in the Snoopi drawing (Figure 3).

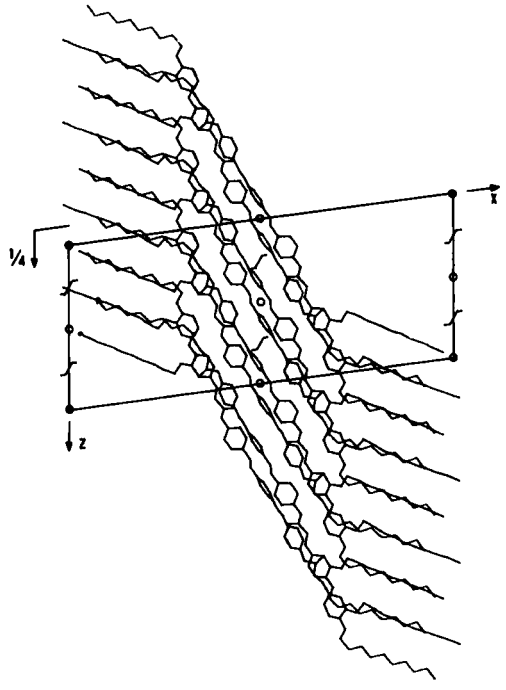



FIGURE 2a Projection of the structure along the y axis.

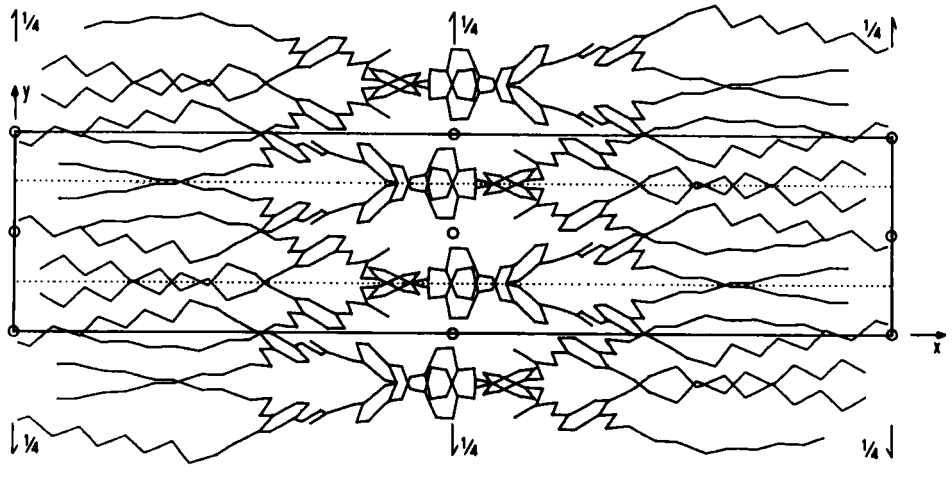



FIGURE 2b Projection of the structure along the z axis.

### Molecular Packing and Arrangement

The cohesion in the crystal is entirely due to numerous Van der Waals forces. Such interactions are quite weak; this is in agreement with the very low density equal to 1.093. There are no intramolecular contacts between the contiguous alkyloxy chains.

The polyaromatic cores are nearly parallel to the xoz plane, with which they

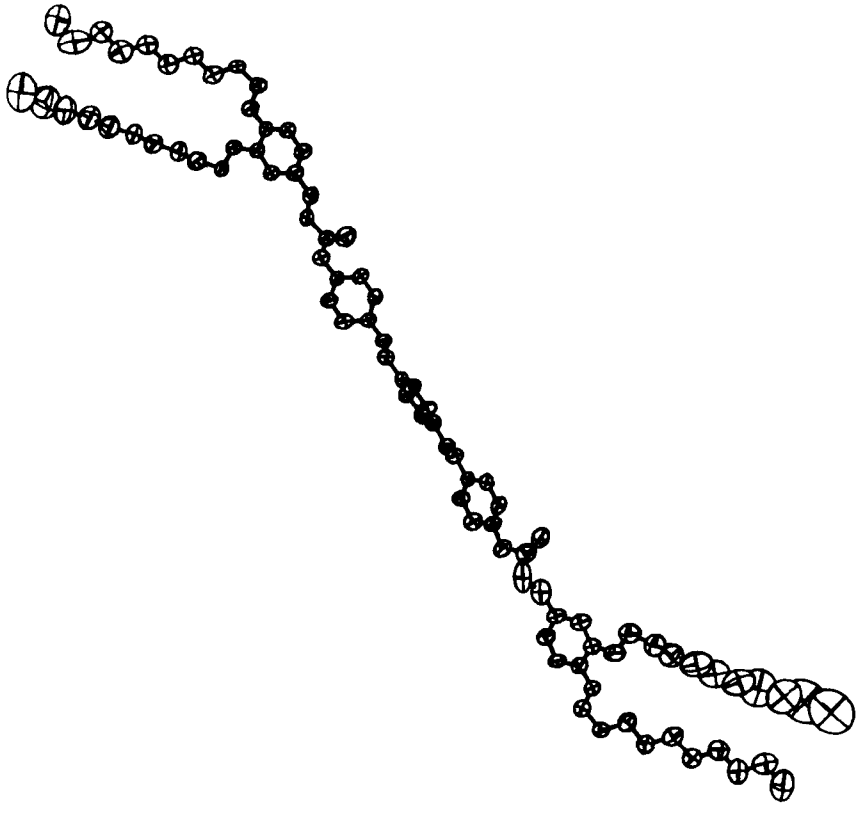


FIGURE 3 Snoopi drawing of the molecule.

make an angle close to only 5°. The alkyloxy chains are quite parallel to the xoz plane. Finally, the molecules are roughly aligned in the same direction parallel to the xoz plane, as can be seen in Figure 2.

There are numerous interactions between the polyaromatic cores related by the centres of symmetry and the $2_1$ axes, located at $x = 0.5$. Only few interactions involve alkyloxy chains: chains 1 and 3 of one molecule are interacting with chains 2 and 4 of neighbouring molecules. The molecules give two-dimensional sheets, parallel to the yz plane, whose thickness is about 43 Å, the length of the a axis. The interactions between sheets involving the terminal methyl groups at $x = 0.0$ and 1.0 are very weak.

The aromatic cores make an angle cose to 75° (tilt angle) with the direction perpendicular to the sheet. The molecular arrangement in Figure 2b is typical of a lamellar structure with segregation of the aliphatic chains and the central polyatomic cores.

It is possible to imagine two domains in the crystal structure of somewhat different density (Figure 2b): the first is relative to the central part of the unit cell corresponding to the polyaromatic central cores with a relatively high local density close to 1.31 $g.cm^{-3}$; the second is relative to the aliphatic terminal chains with a very low local density of 0.93 $g.cm^{-3}$. Such a low density has been observed in the

crystalline *n*-heptane[19] with $d_{cal} = 0.89$. This is in agreement with the very high thermal motion observed for the alkyloxy chains and the very limited number of intermolecular contacts between these chains.

This kind of arrangement, although in the solid state, is perfectly characteristic of a smectic C structure. Such behaviour has been observed in another family of biforked mesogens for short lengths of alkyloxy chains.[7,8] Moreover, the tilt angle in this mesophase is round 50° and the layer thickness is about 36 Å, which is lower than the corresponding value in the crystalline phase (45 Å), probably owing to melting of the chains. Anyway, there is a fairly good correspondence between the molecular structure in the solid state and the supposed one in the lamellar smectic C mesophase.

## CONCLUSION

In the present biforked molecule we have found a striking analogy between the molecular arrangement in the solid state and that in the well-known smectic mesophase. Several structural studies are now in progress on polycatenar mesogens such as the hexagonal ones which exhibit a more complex two-dimensional mesophase. It is to be hoped that indications about the molecular organization may be found directly from the solid phase. This would then help to elucidate the hexagonal phase for which no definitive model has yet been proposed to our knowledge.

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