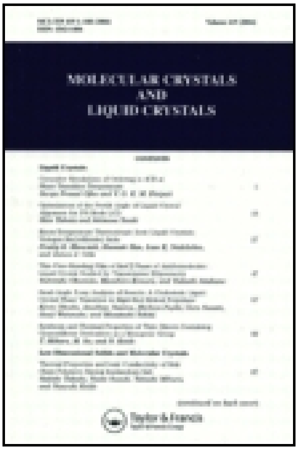

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The Structure of α,ω-bis(4-cyanobiphenyl-4′-oxy)heptane

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The Structure of α,ω-bis(4-cyanobiphenyl-4′-oxy)heptane

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The crystal structure of α,ω-bis(4-cyanobiphenyl-4′-oxy)heptane has been determined from single crystal X-ray diffractometry. The structure is monoclinic, space group $P2_1/n$ with four molecules per unit cell. The cell parameters are $a = 33.737(4)$, $b = 11.084(2)$, $c = 7.106(1)$ Å, $\beta = 94.01(3)°$. The flexible spacer is in the all *trans*-conformation and the long axes of the two mesogen units make an angle of 34° with each other. No indication of grouping between mesogen units belonging to different molecules is detected in the packing analysis.

Keywords: α,ω-*bis(4-cyanobiphenyl-4′-oxy)heptane—single crystal structure, X-ray of siamese twin molecule*

1. INTRODUCTION

Much work in the field of materials displaying thermotropic liquid crystalline properties has been devoted to the study of chain molecules where rigid mesogen units alternate with flexible spacers along the main chain. The reason is that an appro-

$N{\equiv}C{-}Ph{-}Ph{-}O{-}(CH_2)_7{-}O{-}Ph{-}Ph{-}C{\equiv}N$

SCHEME

priate calibration of the mesogenic power of the rigid core and of the conformational flexibility of the spacer allows for planning materials with determined properties of the mesophase, particularly with reference to the thermal range of stability and to the kind of mesophase displayed.[1,2,3]

It has been shown that relatively small structural changes can have important effects on the isotropization temperatures and enthalpies, an example being the well-known even-odd effect. An accurate structural characterization of the polymer chains or of their low molecular weight models is therefore a necessary task for a better understanding of the connection between geometry and liquid-crystalline behaviour.

X-ray single crystal diffractometry gives the most complete picture of molecular geometry, but is seldom applied in this field due to the difficulty of obtaining crystals of proper dimensions and good quality. This is not the case for α,ω-bis(4-cyanobiphenyl-4′-oxy)heptane (see Scheme) which gives rise, upon crystallization from boiling ethyl acetate, to small but well formed needles, thus giving us a favourable opportunity for a complete structural characterization of this namatogenic molecule in the crystalline phase.

2. EXPERIMENTAL AND STRUCTURE DETERMINATION

α,ω-bis(4-Cyanobiphenyl-4′-oxy)heptane was prepared as reported in Reference 4, starting from 4-hydroxy-4′-cyanobiphenyl and α,ω-dibromoheptane. White small needles were obtained after recrystallization from boiling ethyl acetate. The chosen crystal was approximately 0.3 × 0.05 × 0.05 mm.

Intensity measurements were collected on an Enraf-Nonius CAD-4 automatic diffractometer at room temperature with graphite monochromated MoKα radiation, using the θ/2θ scan technique. Cell dimensions were obtained by least-squares refinement of 24 reflections in the range $8° \leq \theta \leq 18°$. The structure is monoclinic, space group $P2_1/n$, with four molecules per unit cell and cell parameters a = 33.737(4), b = 11.084(2), c = 7.106(1) Å, β = 94.01(3)°. 3741 independent reflections were collected up to $\theta_{max} = 28°$, and 2438 were considered observed having $I \geq 2\sigma(I)$. Lorentz and polarization corrections were applied. The structure was solved with MULTAN-80[5] and successive Fourier syntheses, while refinement was carried out with SHELX-76.[6] Anisotropic thermal parameters were introduced for all non-hydrogen atoms and difference Fourier syntheses were used to locate, in the final stage, the hydrogen atoms. The refinement procedure converged to $R = 0.052$ and $R_w = 0.054$.

3. RESULTS AND DISCUSSION

The final fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table I. Bond distances, angles and selected torsion angles are given in Table II. All geometrical calculations were carried out with PARST program.[7]

TABLE I

Fractional Atomic Coordinates ($\times 10^4$) for Non-H Atoms and Equivalent Isotropic Temperature Factors B (Å^2)

ATOM	X	Y	Z	$B_{eq.}$
O(1)	5371(1)	1607(2)	4719(3)	5.3(2)
O(2)	6918(1)	874(2)	-6320(3)	6.5(2)
N(1)	8771(1)	3233(3)	-17943(4)	8.5(3)
N(2)	3569(1)	5076(3)	15880(4)	9.2(3)
C(1)	5558(1)	2368(3)	3409(5)	6.7(3)
C(2)	5737(1)	1541(3)	2021(5)	6.8(3)
C(3)	5946(1)	2231(3)	518(5)	6.4(3)
C(4)	6148(1)	1384(3)	-794(5)	6.7(3)
C(5)	6363(1)	2023(3)	-2317(5)	6.6(3)
C(6)	6561(1)	1131(3)	-3620(5)	6.5(3)
C(7)	6768(1)	1797(3)	-5150(5)	6.8(3)
C(8)	7138(1)	1221(3)	-7787(4)	6.1(3)
C(9)	7216(1)	2391(3)	-8247(5)	6.5(3)
C(10)	7457(1)	2621(3)	-9724(4)	6.6(3)
C(11)	7615(1)	1699(3)	-10741(4)	5.9(3)
C(12)	7522(1)	524(3)	-10276(4)	6.0(3)
C(13)	7287(1)	282(3)	-8807(4)	6.2(3)
C(14)	7876(1)	1967(3)	-12291(4)	5.6(2)
C(15)	8146(1)	2905(3)	-12116(4)	6.0(3)
C(16)	8386(1)	3181(3)	-13562(4)	6.2(3)
C(17)	8352(1)	2533(3)	-15228(4)	5.9(3)
C(18)	8089(1)	1581(3)	-15410(4)	6.5(3)
C(19)	7854(1)	1301(3)	16043(4)	6.8(3)
C(32)	8588(1)	2896(3)	-16754(5)	6.9(3)
C(20)	5169(1)	2116(3)	6111(4)	6.9(3)
C(21)	4979(1)	1308(3)	7226(5)	7.1(3)
C(22)	4759(1)	1717(3)	8655(4)	7.0(3)
C(23)	4719(1)	2943(3)	9011(4)	6.2(3)
C(24)	4916(1)	3738(3)	7895(4)	6.3(3)
C(25)	5141(1)	3333(3)	6458(4)	6.3(3)
C(26)	4467(1)	3374(3)	10492(4)	5.8(3)
C(27)	4466(1)	2789(3)	12228(4)	6.4(3)
C(28)	4232(1)	3191(3)	13622(4)	7.0(3)
C(29)	3995(1)	4190(3)	13309(4)	6.5(3)
C(30)	3985(1)	4774(3)	11567(5)	6.8(3)
C(31)	4225(1)	4368(3)	10199(4)	6.7(3)
C(33)	3754(1)	4661(3)	14744(5)	7.4(3)

A perspective view of the molecule with the atomic numbering scheme is shown in Figure 1. The alkyl chain shows an all *trans*-conformation, the maximum deviation from the least-squares plane passing through the nine chain atoms being 0.047(4) Å. The long axes (O(1) . . . C(33) and O(2) . . . (32)) of the rigid groups are coplanar with the chain plane and are tilted at a mean angle of 17.4° relative to the chain axis (O(1) . . . O(2)) while making an angle of 34.2° with each other. This is a rather low value when compared with expected angles in the range 50°–60° in the case of odd membered spacers in extended conformation.[8,9] The reason is to be found in a distorted geometry of the connections between the spacer and the two cyanobiphenyl groups as results from the difference between O(2)-C(8)-C(9) (124.7°) and O(2)-C(8)-C(13) (115.0°) bond angles and, symmetrically, between O(1)-C(20)-C(25) (125.5°) and O(1)-C(20)-C(21) (115.1°) bond angles. This effect is still enhanced by the large bond angles at O(1) and O(2), 119.5° and 118.1° respectively, and the narrow angles at C(1) and C(7), 106.4° and 106.5°. The

TABLE II

Molecular Dimensions

SELECTED BOND LENGTHS (Å)

O(1)	- C(1)	1.435(4)
O(1)	- C(20)	1.361(4)
O(2)	- C(7)	1.433(4)
O(2)	- C(8)	1.375(4)
N(1)	- C(33)	1.152(5)
N(2)	- C(32)	1.144(5)
C(1)	- C(2)	1.504(5)
C(2)	- C(3)	1.524(5)
C(3)	- C(4)	1.519(5)
C(4)	- C(5)	1.518(5)
C(5)	- C(6)	1.519(5)
C(6)	- C(7)	1.508(5)
C(11)	- C(14)	1.487(4)
C(17)	- C(32)	1.447(5)
C(23)	- C(26)	1.478(4)
C(29)	- C(33)	1.444(5)

SELECTED BOND ANGLES (°)

C(1)	- O(1)	- C(20)	119.5(3)
C(7)	- O(2)	- C(8)	118.1(3)
O(1)	- C(1)	- C(2)	106.4(3)
C(1)	- C(2)	- C(3)	112.4(3)
C(2)	- C(3)	- C(4)	111.7(3)
C(3)	- C(4)	- C(5)	114.0(3)
C(4)	- C(5)	- C(6)	113.1(3)
C(5)	- C(6)	- C(7)	113.1(3)
O(2)	- C(7)	- C(6)	106.5(3)
O(2)	- C(8)	- C(13)	115.0(3)
O(2)	- C(8)	- C(9)	124.7(3)
C(10)	- C(11)	- C(14)	120.6(3)
C(12)	- C(11)	- C(14)	121.3(3)
C(11)	- C(14)	- C(19)	121.7(3)
C(11)	- C(14)	- C(15)	120.3(3)
C(16)	- C(17)	- C(32)	118.7(3)
C(18)	- C(17)	- C(32)	121.7(3)
N(2)	- C(32)	- C(17)	177.1(4)
O(1)	- C(20)	- C(25)	125.5(3)
O(1)	- C(20)	- C(21)	115.1(3)
C(22)	- C(23)	- C(26)	120.9(3)
C(24)	- C(23)	- C(26)	121.6(3)
C(23)	- C(26)	- C(31)	121.0(3)
C(23)	- C(26)	- C(27)	121.2(3)
C(28)	- C(29)	- C(33)	121.7(3)
C(30)	- C(29)	- C(33)	118.6(3)
N(1)	- C(33)	- C(29)	177.6(4)

SELECTED TORSION ANGLES (°)

C(1)	-O(1)	-C(20)	-C(25)	-3.3(5)
C(20)	-O(1)	-C(1)	-C(2)	-177.7(3)
C(7)	-O(2)	-C(8)	-C(9)	-1.8(4)
C(7)	-O(2)	-C(8)	-C(13)	177.3(3)
C(8)	-O(2)	-C(7)	-C(6)	-177.0(3)
O(1)	-C(1)	-C(2)	-C(3)	179.5(3)
C(1)	-C(2)	-C(3)	-C(4)	176.3(3)
C(2)	-C(3)	-C(4)	-C(5)	-179.7(3)
C(3)	-C(4)	-C(5)	-C(6)	-179.6(3)
C(4)	-C(5)	-C(6)	-C(7)	179.1(3)
C(5)	-C(6)	-C(7)	-O(2)	-176.6(3)
C(10)	-C(11)	-C(14)	-C(15)	38.1(4)
C(24)	-C(23)	-C(26)	-C(31)	39.6(5)

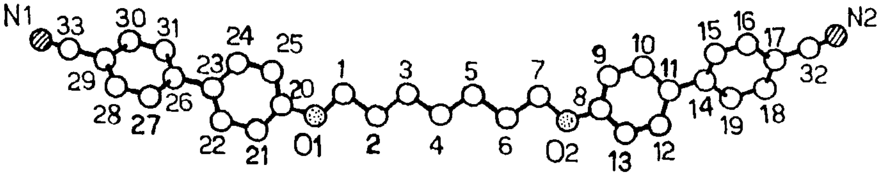

FIGURE 1 The molecule projected on the least-squares plane passing through the nine atoms of the spacer. The atom numbering scheme is also shown.

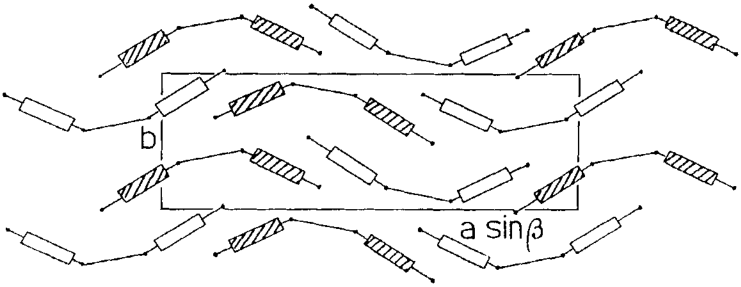

FIGURE 2 Schematical representation of packing viewed along the *c* axis. Mesogen units are represented by rods while flexible spacers are represented by straight lines. Shading is adopted to distinguish between molecules with opposite orientations of the concavity.

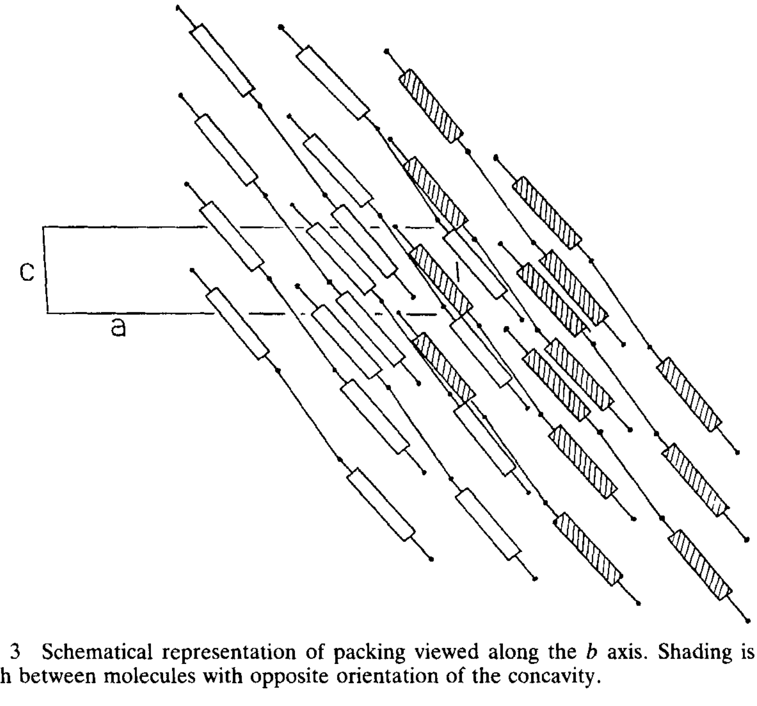

FIGURE 3 Schematical representation of packing viewed along the *b* axis. Shading is adopted to distinguish between molecules with opposite orientation of the concavity.

geometry we find at the ether linkage is in accord with an electron diffraction study of anisole.[10]

The two mesogen units have practically the same geometry; the mean dihedral angle between the two phenyl rings is 39°. Bond lengths and angles of the cyanobiphenyl moieties are in agreement with standard values.

No extra short intermolecular contact is detected; in Figure 2 and Figure 3 we report the crystal packing viewed along *c* and *b* axes respectively. Rigid cores are represented by rods and the all-*trans* spacer is represented by a straight line. Shaded molecules are drawn in order to distinguish between opposite orientations of arched molecules, as is particularly evident in Figure 2. There is no indication of grouping between mesogen units belonging to different molecules.

4. SUPPLEMENTARY MATERIALS

Tables of anisotropic thermal parameters for non-H atoms, a list of fractional coordinates for H-atoms, and a list of observed and calculated structure factors are available by contacting Gordon and Breach, 5301 Tacony Street, Drawer 330, Philadelphia, PA 19137, USA. Please mark your envelope "attention MCLC Supplementary Materials."

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