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Crystal structure of the mesogenic alkene monomer, 3-[4-(4′-ethylbiphenyl)]-1-propene

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The crystal and molecular structures of the mesogenic monomer 3-[4-(4′-ethylbiphenyl)]-1-propene, molecular formula $CH_3-CH_2-C_6H_4-C_6H_4-CH_2-CH{=}CH_2$, has been determined by X-ray diffraction analysis at 293(2) K. The compound crystallizes in the form of a non-centrosymmetric monoclinic system, space group *Pc*, with two molecules per cell. The cell parameters are $a = 13.90(5)$ Å, $b = 5.75(1)$ Å, $c = 9.54(5)$ Å and $\beta = 116.1(3)°$. Refinement leads to $R = 0.0554$. Both phenyl rings adopt boat conformations and are nearly coplanar. The molecules form a smectic-like layer structure in the crystalline state.

1. Introduction

X-ray measurements have shown that the positional and orientational ordering in highly ordered crystalline smectic phases is more comparable with the ordering in the solid state than with the structures of the fluid smectic phases and the nematic phase. To date, the crystal structures of very few mesogenic compounds exhibiting highly ordered smectic phases have been reported. Most of the X-ray structure analyses of mesogenic materials have used materials which form fluid smectic phases (SmA and SmC) or a nematic phase [1]. In contrast, the title compound exhibits the crystalline B phase over a remarkably broad temperature range.

A series of new alkene monomers have been synthesized and reported [2]. The title compound 3-[4-(4′-ethylbipenyl)]-1-propene (MS3DBT2) has an alkene group linked to a biphenyl mesogenic group in the 4′ position. Typical DSC thermograms obtained on heating and cooling the monomer MS3DBT2 were reported and no crystallization was observed even on cooling to −30°C [2]. The optical textures have been observed under crossed polarizers using a polarizing microscope of magnification 150X. The transition temperatures agree well with reported values and we observe a characteristic mosaic texture indicative of the crystalline B phase. The reported transition temperatures [2] are:

Heating scans: CrB 63.0°C (11.3/33.6) I,
Cooling scans: I 44.6°C (13.1/41.2) CrB.

The thermodynamic parameters associated with phase transition ($\Delta H/\Delta S$) are shown in parentheses in kJ mol^{-1} and J mol^{-1} K, respectively.

2. Experimental

2.1. *Crystal data*

The title compound MS3DBT2 was prepared as described by Chang-Chien [2], who kindly supplied the compound. Transparent plate-shaped crystals were obtained by slow evaporation at 296(2) K of a methanolic solution; the crystal size was $0.5 \times 0.3 \times 0.2$ mm^3.

Lattice dimensions were determined at 293(2) 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 [3]. Data collection at 293(2) K was done by CAD-4 EXPRESS having θ values $1.63° < \theta < 24.97°$. The index ranges were found to be $-16 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 6$, $0 \leqslant l \leqslant 11$. Data reduction was done by XCAD-4 [4]. MoK$_\alpha$ radiation and a graphite monochromator were used to collect 1279 reflections on ω-2θ scan mode, of which 306 were treated as observed with $I > 2\sigma(I)$. The selected space group is based on the reflections, which are systematically absent.

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2.2. *Structure determination and refinement*

The structure of MS3DBT2 was solved by the direct methods of SHELXS-97 [5]. The best E-map of MS3DBT2 depicts the whole molecule. The structure was refined by a full-matrix lease squares method on F^2 by using the program SHELXL-97 [6] with an individual isotropic temperature factor to an R-value of 0.14. The introduction of individual anisotropic temperature factors reduced the R-value to 0.09. In this solution some constraints must be introduced and the atoms have high thermal parameters but no evidence of disorder is present. The distances between the atoms C2–C3, C16–C17, C15–C16 and C12–C15 were restrained to a target value. The positions of the hydrogen atoms were inserted from the molecular geometry around the carbon atoms. The H atoms were allowed to ride on their parent atom with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}$ (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(6). The atomic scattering factors were taken from the International Tables for Crystallography [7]. Finally we obtained an R-value of 0.0554 and $r_w = 0.1058$. A difference Fourier map at this stage showed no electron density greater than 0.092 e Å^{-3}. The Flack x parameter was 10(0) and an absolute structure could not be determined reliably [8]. Detailed crystal structure data of solution and refinement are summarized in table 1.

3. Results and discussion

3.1. *Molecular conformation*

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in table 2. Anisotropic parameters (U_{ij}) are listed in table 3. Most of the atoms have higher thermal parameters, especially the terminal atom C17. Figure 1 represents the ORTEP [9] diagram of the molecular structure of MS3DBT2 with thermal ellipsoids at 30% probability and the H atoms have an arbitrary radius. Bond lengths and bond angles are normal within the limits of error and are listed in table 4. All the calculations were performed using PARST [10].

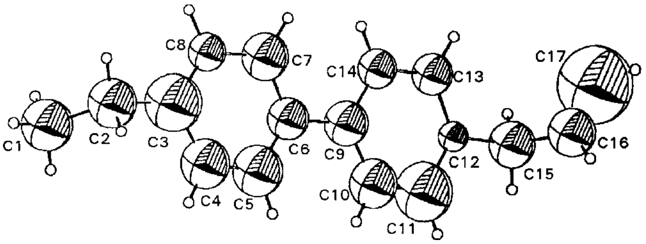

Figure 1. Perspective drawing of an MS3DBT2 molecule showing the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms have an arbitrary radius.

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

Crystal data	
Molecular formula	$C_{17}H_{18}$
Molecular mass	222.31 g mol^{-1}
Temperature K	293(2) K
Wavelength (MoK$_\alpha$)	0.7093/Å
Crystal system	Monoclinic
Lattice type	Non-centrosymmetric
Space group	*Pc*
Form/habit	Block
Crystal size	$0.5 \times 0.3 \times 0.2$ mm^3
Cell parameters from 25 reflections	$a = 13.90(5)$ Å $b = 5.75(10)$ Å $\beta = 116.1(3)°$ $c = 9.54(5)$ Å
V_c	685(5)/Å^3
Z	2
D_x	1.079 Mg m^{-3}
D_m	not measured
Data collection	
θ-range for data collection	1.63° to 24.97°
Index ranges	$-16 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 6$, $0 \leqslant l \leqslant 11$
Absorption coefficient	0.060 mm^{-1}
$F(0\,0\,0)$	240
Reflections collected	1279
No. of independent reflections	1279 [R(int) = 0.0000]
No. of observed reflections	306
No. of parameters/restraints	154/6
Refinement	
Refinement method	Full-matrix least-squares on F^2
Max. shift	0.049 esd
W	$1/[\sigma^2(F_o^2) + (0.0495P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0554$, $WR_2 = 0.1058$
R indices (all data)	$R_1 = 0.3096$, $WR_2 = 0.1781$
Absolute structure parameter	10(10)
Largest diffraction peak and hole	0.092 and -0.088 e Å^{-3}

The puckering parameters of the six-membered rings, calculated using the method of Cremer and Pople [11], appear in table 5. A unique mean plane is defined for a general monocyclic puckering ring. The geometry of the puckering relative to this plane is described by an amplitude and phase coordinates. For the six-membered ring, there are three puckering degrees of freedom. These are described by a single amplitude—phase pair (q_2, ϕ_2) and a single puckering coordinate q_3. Alternatively, these coordinates may be replaced 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

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

Atom	x	y	z	U_{eq}
C1	0.415(2)	0.530(6)	−0.374(3)	0.189(9)
C2	0.4982(16)	0.344(5)	−0.335(2)	0.195(14)
C3	0.591(2)	0.298(3)	−0.198(3)	0.142(10)
C4	0.6789(17)	0.458(4)	−0.134(3)	0.124(8)
C5	0.7642(15)	0.446(3)	0.011(3)	0.118(8)
C6	0.7777(15)	0.268(4)	0.107(2)	0.103(7)
C7	0.7023(19)	0.092(4)	0.052(2)	0.141(9)
C8	0.6101(18)	0.126(5)	−0.090(3)	0.152(9)
C9	0.8705(19)	0.242(4)	0.263(2)	0.091(6)
C10	0.9506(18)	0.402(4)	0.316(2)	0.117(8)
C11	1.0339(19)	0.397(3)	0.462(2)	0.141(9)
C12	1.0440(13)	0.209(5)	0.5517(18)	0.110(7)
C13	0.9718(16)	0.032(4)	0.505(3)	0.134(8)
C14	0.8831(14)	0.054(4)	0.358(2)	0.129(8)
C15	1.1391(15)	0.194(4)	0.711(2)	0.168(11)
C16	1.221(3)	0.045(7)	0.719(4)	0.28(2)
C17	1.226(3)	−0.113(7)	0.801(4)	0.34(2)

$Q_3 = Q \cos \theta$. This coordinate system permits the mapping of all types of puckering (for a given amplitude Q) on the surface of a sphere. Here, we have found that the polar positions correspond to a boat conformation with $q_3 = 0$ and $Q_2 = Q$. Ring A is defined by the atoms from C_3 to C_8 and ring B is defined by the atoms from C_9 to C_{14}.

The normals to the least-squares mean planes through the alkene group (C_1–C_3) and the phenyl ring A make a dihedral angle of 106.47(1.66)°. The corresponding angle with ring B was found to be 107.56(1.64)°. The least-squares mean plane calculated through the spacer atoms (C_{12}–C_{17}) makes an angle of 78.45(1.58)° with the adjacent ring B and with ring A it was found to be 79.45(1.59)°. The two phenyl rings are nearly coplanar with a dihedral angle of 1.49(4)°.

3.2. *Molecular packing*

The packing of the molecules in the unit cell looking down the *a*, *b* and *c* axes are shown in figures 2, 3 and 4, respectively. The molecules are organized in parallel sheets as observed in figures 3 and 4. No overlapping of molecules or atoms occurs in the crystalline state. The projection of the long molecular axis in the (0 0 1) plane forms an angle of approximately 64° with the *c* axis.

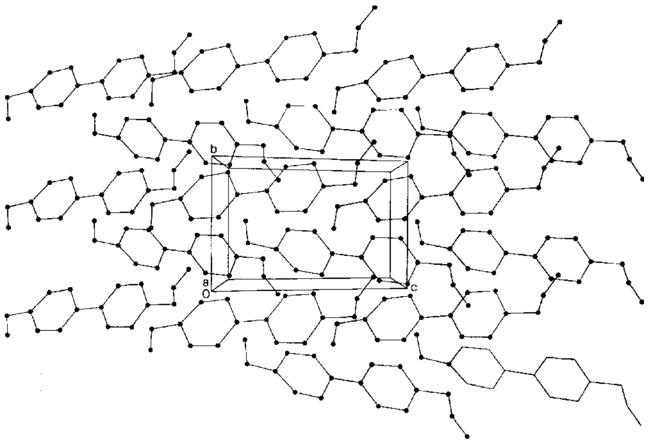

Figure 2. Molecular packing along [1 0 0].

Table 3. Anisotropic displacement parameters U_{ij} ($\times 10^{-3}$) for non-hydrogen atoms with e.s.d values 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}
C1	0.19(2)	0.21(3)	0.158(19)	−0.031(18)	0.077(18)	−0.02(2)
C2	0.17(2)	0.20(3)	0.099(15)	−0.029(17)	−0.037(15)	−0.07(2)
C3	0.24(3)	0.033(9)	0.19(2)	−0.002(15)	0.13(2)	0.019(16)
C4	0.18(2)	0.10(2)	0.136(18)	0.034(17)	0.108(17)	−0.005(17)
C5	0.19(2)	0.040(9)	0.15(2)	0.018(13)	0.101(19)	0.019(11)
C6	0.127(17)	0.079(17)	0.116(18)	−0.045(14)	0.066(16)	−0.034(15)
C7	0.16(2)	0.089(17)	0.126(16)	−0.028(14)	0.020(15)	−0.046(16)
C8	0.105(16)	0.14(2)	0.20(2)	−0.055(19)	0.050(16)	−0.058(15)
C9	0.144(18)	0.057(13)	0.106(16)	−0.006(11)	0.087(16)	−0.005(12)
C10	0.17(2)	0.103(18)	0.110(17)	0.025(15)	0.091(16)	−0.008(16)
C11	0.25(2)	0.071(14)	0.095(15)	0.011(13)	0.067(15)	−0.033(15)
C12	0.066(10)	0.17(2)	0.084(12)	−0.016(15)	0.025(10)	−0.017(14)
C13	0.123(17)	0.103(18)	0.16(2)	0.007(15)	0.044(17)	0.017(15)
C14	0.111(17)	0.136(17)	0.144(18)	0.028(15)	0.059(15)	−0.050(12)
C15	0.156(19)	0.17(2)	0.20(3)	0.040(17)	0.102(19)	0.080(16)
C16	0.17(2)	0.34(6)	0.28(4)	0.06(3)	0.05(2)	−0.02(3)
C17	0.43(4)	0.29(4)	0.25(3)	−0.02(3)	0.11(3)	−0.16(4)

Table 4. Bond distances and angles with e.s.d values in parentheses.

Bond	Length/Å	Angle	Value/°
C1–C2	1.52(3)	C3–C2–C1	121(2)
C2–C3	1.512(19)	C8–C3–C4	107.3(19)
C3–C8	1.37(3)	C8–C3–C2	132(2)
C3–C4	1.43(3)	C4–C3–C2	120(2)
C4–C5	1.37(2)	C5–C4–C3	126.5(19)
C5–C6	1.33(2)	C6–C5–C4	122(2)
C6–C7	1.38(2)	C5–C6–C7	117(2)
C6–C9	1.482(16)	C5–C6–C9	124.2(17)
C7–C8	1.41(3)	C7–C6–C9	119(2)
C9–C10	1.36(3)	C6–C7–C8	119(2)
C9–C14	1.37(2)	C3–C8–C7	128(2)
C10–C11	1.36(3)	C10–C9–C14	116(2)
C11–C12	1.35(2)	C10–C9–C6	121.0(16)
C12–C13	1.36(3)	C14–C9–C6	123(2)
C12–C15	1.515(17)	C9–C10–C11	123.9(19)
C13–C14	1.41(2)	C12–C11–C10	117.9(19)
C15–C16	1.40(2)	C11–C12–C13	122.4(17)
C16–C17	1.18(2)	C11–C12–C15	119(2)
		C13–C12–C15	119(2)
		C12–C13–C14	117(2)
		C9–C14–C13	121.9(19)
		C16–C15–C12	115(2)
		C17–C16–C15	108(4)

Table 5. Ring puckering parameters (Å, °) of the phenyl rings with e.s.d values in parentheses.

Ring	q_2	q_3	Q	θ
A[a]	0.0815(2)	−0.0297(2)	0.0867(2)	110.05(1)
B[a]	0.0517(2)	0.0214(1)	0.0560(2)	67.49(1)

[a] Ring A is defined by the atoms from C_3 to C_8; ring B is defined by the atoms from C_9 to C_{14}.

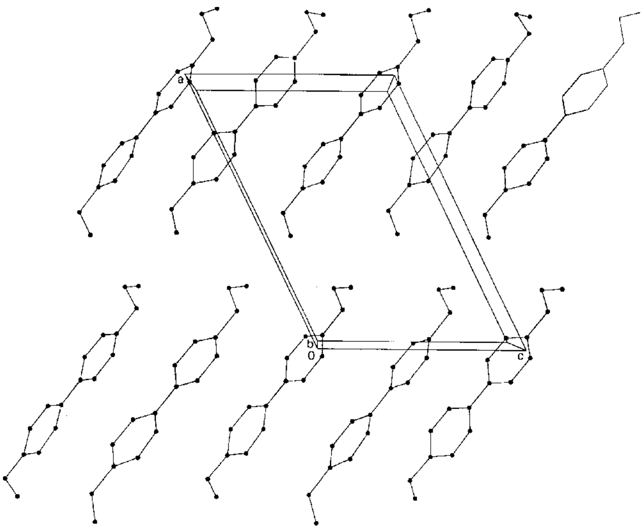

Figure 3. Molecular packing along [0 1 0].

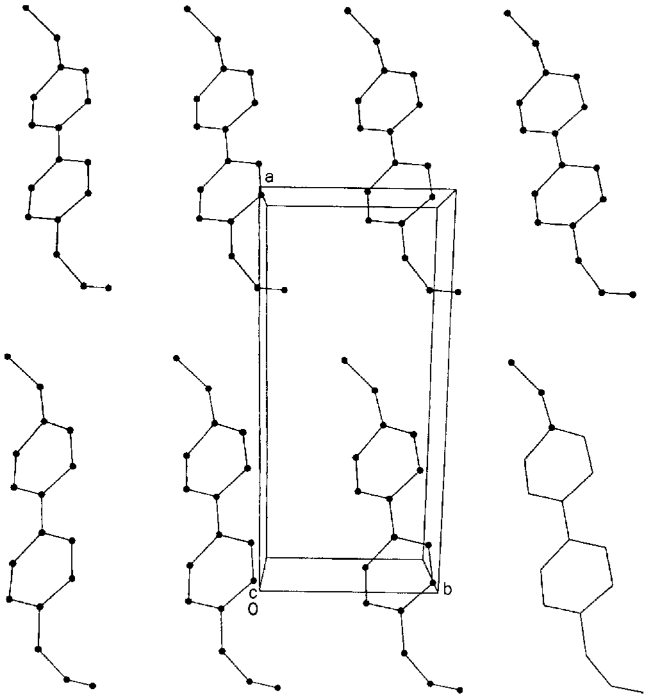

Figure 4. Molecular packing along [0 0 1].

This type of layered structure clearly indicates the crystal B phase of the title compound. Since the compound contains no polar groups, the arrangement in the crystalline state is strongly dominated by repulsion potentials.

It is well known that in the smectic B cell, the intermolecular distances can be assumed to be equivalent to the lattice dimensions *a* and *b*, whereas the molecular length is related to the thickness of the layer along the crystallographic *c* axis [12]. The length of the molecule in the crystalline state is 12.45 Å. The layer spacing in the mesophase has been obtained from an X-ray diffraction pattern and was found to be 12.6 Å [2]. The layer spacing, comparable to the calculated length of the molecule, shows that the molecules form a smectic B-like arrangement within the layers.

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