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Two crystal forms of mesogenic bis(4′-cyanobiphenyl-4-yl) butanedioate

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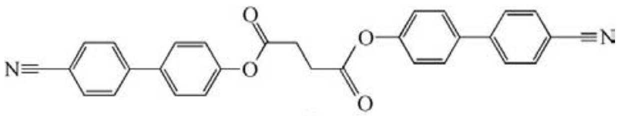
The title compound, $C_{30}H_{20}N_2O_4$, exhibits a nematic phase in the wide temperature range between 498.5 and 538.6 K, in spite of the short linker moiety. Two crystal forms have been found. In both forms, the molecule is centrosymmetric. Form I has a planar biphenyl group, while form II has a twisted biphenyl group with a twist angle of 34.75 (6)°. The packing modes are also different. In form I the long molecular axes are tilted with respect to each other at about 30°, while in form II the long molecular axes have an almost parallel arrangement.

Comment

Dimeric liquid crystals have attracted considerable attention because they are regarded as model compounds for polymeric liquid crystals. Previously, we reported the crystal structures of two series, *viz.* α,ω-bis(4-cyanobiphenyl-4′-yloxycarbonyl)propane and -hexane, and α,ω-bis(4-cyanobiphenyl-4′-yl)octane and -nonane (Hori *et al.*, 2004). The molecules of the ester compounds are centrosymmetric, while the molecular structures were asymmetric for the latter two compounds with alkyl chains as linkages.

In order to investigate the short limit of the linkage for liquid crystalline behaviour, we synthesized the title compound, (I), which exhibits a nematic phase in the wide temperature range between 498.5 and 538.6 K. We found two crystal forms, denoted I and II. Form I, with an oval plate shape, was obtained predominantly, while form II, with a rod shape, was only obtained once. Both forms were apparently stable between 200 K and room temperature.



(I)

As shown in Fig. 1, the molecules are centrosymmetric. The molecules are fully extended with *trans* conformations in the

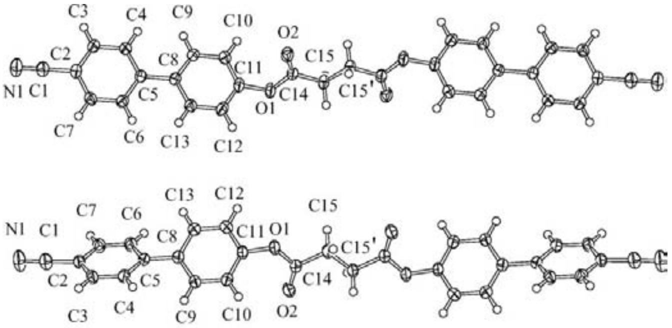


Figure 1
The molecular structures of forms I (top) and II (bottom) of (I), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Primed atoms are related by symmetry codes $(-x+1, -y, -z)$ and $(-x+1, -y, -z+1)$, respectively.

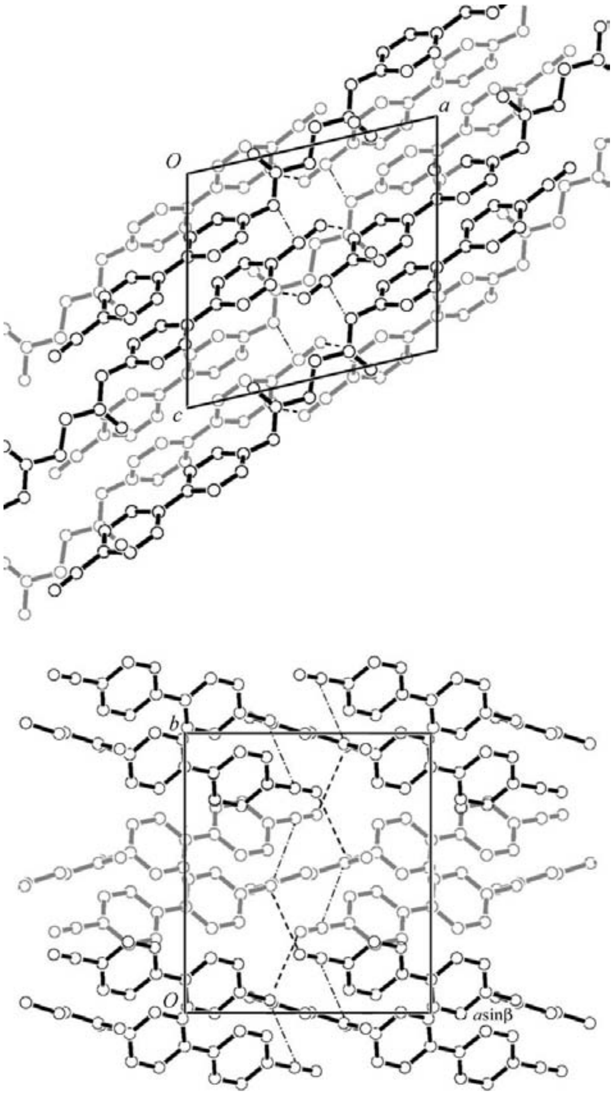


Figure 2
The crystal structure of form I of (I), viewed along the *b* (top) and *c* (bottom) axes. Black and grey molecules denote corresponding molecules in the two parts. Broken lines denote the N1···C14$(x-1, -y+\frac{1}{2}, z+\frac{1}{2})$ distance, and dotted and dashed lines denote the O1···C1$(-x, -y, -z+1)$ distance (see *Comment*). H atoms have been omitted for clarity.

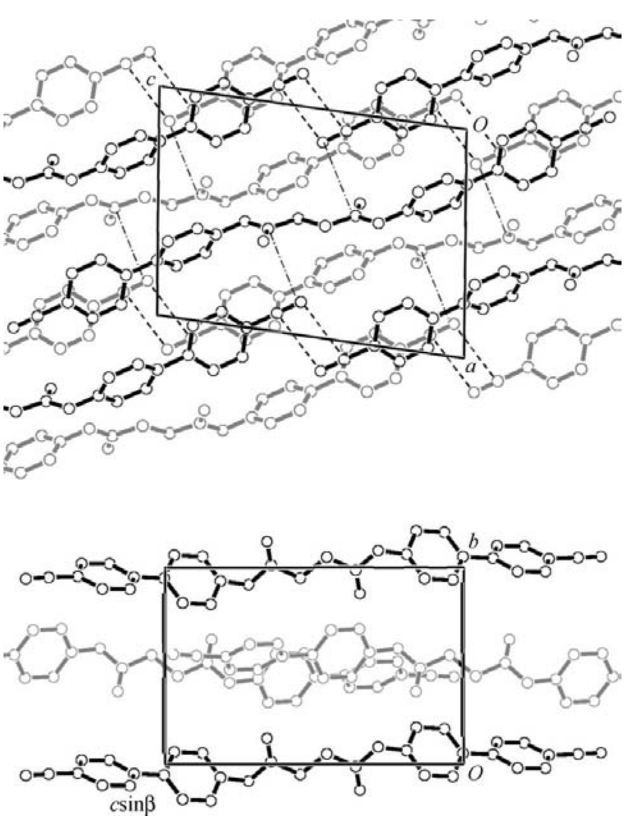


Figure 3
The crystal structure of form II of (I), viewed along the b (top) and a (bottom) axes. Black and grey molecules denote corresponding molecules in the two parts. Dashed lines denote the N1···C1($-x+2$, $-y$, $-z+3$) distance, and dotted and dashed lines denote the N1···C14($-x+2$, $-y$, $-z+2$) distance (see *Comment*). H atoms have been omitted for clarity.

alkyl chain linkages. However, the biphenyl moieties are quite different, with an almost planar biphenyl group [dihedral angle = 4.65 (10)°] in form I and a twisted biphenyl group [dihedral angle = 34.75 (6)°] in form II.

The packing modes are also different. In form I, the long molecular axes are tilted with respect to each other at about 30°, as shown in Fig. 2. Here, the nearest groups to the CN group are the ester linkages: 3.189 (2) Å for N1···C14($x-1$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$), 3.261 (2) Å for N1···O1($x-1$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$), 3.356 (2) Å for O1···C1($-x$, $-y$, $-z+1$), 3.595 (2) Å for N1···O2($x-1$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$) and 3.620 (2) Å for N1···O1($-x$, $-y$, $-z+1$).

On the other hand, the long molecular axes have an almost parallel arrangement in form II, as shown in Fig. 3. An antiparallel arrangement of CN groups, with a distance of 3.260 (3) Å for N1···N1($-x+2$, $-y$, $-z+3$) and 3.267 (2) Å for N1···C1($-x+2$, $-y$, $-z+3$), is found in the sheet parallel to the ac plane. In addition, short distances are found between a CN group and an ester moiety: 3.1672 (18) Å for N1···O2($-x+2$, $-y$, $-z+2$) and 3.5156 (19) Å for N1···C14($-x+2$, $-y$, $-z+2$).

Differential scanning calorimetry (DSC) showed no phase transitions between room temperature and the melting point of form I of (I) at 498.5 K. Unfortunately, DSC could not be carried out for form II due to the very small number of crystals. Microscopic observation confirmed that form II showed no change until the melting point, which was 1–2 K lower than that of form I, meaning that form I is more stable throughout the temperature range from room temperature to the melting point. This result is in accordance with the density rule, stating that the most efficiently packed structure is the most stable form (Bernstein, 2002), a direct consequence of the closest packing principle (Kitaigorodsky, 1961).

For isolated molecules, the most stable conformation of the biphenyl moiety was obtained when the dihedral angle was 40° by AM1 calculation (*MOPAC2002*; Fujitsu, 2002). The heat of formation for the planar conformation was higher by 4.5 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). Thus, the disadvantage of the molecular stability of form I is compensated by the more efficient packing of its planar biphenyl moieties.

On melting, a nematic phase appeared, as confirmed by the Schlieren texture, and the material then transformed to an isotropic phase at 538.6 K. The transition enthalpy was 37.3 kJ mol^{-1} for form I to nematic and 6.5 kJ mol^{-1} for nematic to isotropic.

Experimental

The title compound was synthesized as described previously (Hori *et al.*, 2004). Three kinds of crystals, *viz.* oval plate, needle and rod, were obtained by slow evaporation from dichloromethane with a small amount of methanol. Cell dimensions were the same for the oval plate and needle crystals and these were denoted form I. The rod-shaped crystals, obtained only once, had different cell dimensions and were denoted form II. DSC was carried out on a DSC-22C (Seiko) and microscopic observation was performed on a POM microscope (Olympus) equipped with an FP-82 hot stage (Mettler).

Form I of compound (I)

Crystal data

$C_{30}H_{20}N_2O_4$
$M_r = 472.48$
Monoclinic, $P2_1/c$
$a = 10.478$ (3) Å
$b = 11.6064$ (11) Å
$c = 9.590$ (3) Å
$\beta = 103.06$ (2)°
$V = 1136.1$ (5) Å^3
$Z = 2$
Cu $K\alpha$ radiation
$\mu = 0.75$ mm^{-1}
$T = 200$ (2) K
0.6 × 0.4 × 0.1 mm

Data collection

Rigaku AFC-7R diffractometer
Absorption correction: ψ scan
(North *et al.*, 1968)
$T_{\min} = 0.654$, $T_{\max} = 0.932$
2587 measured reflections
2033 independent reflections
1955 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
3 standard reflections
every 150 reflections
intensity decay: 0.3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.128$
$S = 1.12$
2033 reflections
164 parameters
H-atom parameters not refined
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Form II of compound (I)

Crystal data

$C_{30}H_{20}N_2O_4$	$V = 1160.0$ (2) Å^3
$M_r = 472.48$	$Z = 2$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 9.9235$ (11) Å	$\mu = 0.74$ mm^{-1}
$b = 8.7879$ (10) Å	$T = 200$ (2) K
$c = 13.4152$ (17) Å	0.5 × 0.2 × 0.1 mm
$\beta = 97.452$ (10)°	

Data collection

Rigaku AFC-7*R* diffractometer	1928 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{\rm int} = 0.044$
$T_{\rm min} = 0.819$, $T_{\rm max} = 0.929$	3 standard reflections every 150 reflections
2846 measured reflections	intensity decay: −3.1%
2097 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	164 parameters
$wR(F^2) = 0.105$	H-atom parameters not refined
$S = 1.04$	$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
2097 reflections	$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

H atoms were positioned geometrically and treated as riding, with C—H = 0.95–0.99 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

For both compounds, data collection: *PROCESS* (Rigaku, 1996); cell refinement: *PROCESS*; data reduction: *PROCESS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *TEXSAN* (Molecular Structure Corporation & Rigaku, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3008). Services for accessing these data are described at the back of the journal.

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