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Bis(4-butoxyphenyl) Terephthalate

Roberto Centore and Angela Tuzi

Dipartimento di Chimica, Università di Napoli 'Federico II', Via Mezzocannone 4, 80134 Napoli, Italy. E-mail: centore@chemna.dichi.unina.it

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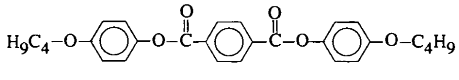
Abstract

The crystal and molecular structures of nematogenic bis(4-butoxyphenyl) terephthalate, $C_{28}H_{30}O_6$, are reported. The molecular structure, determined by X-ray diffraction, is very different from that of the same compound reported on the basis of solid-state NMR analysis [Uryu & Kato (1988). *Macromolecules*, **21**, 378–384]. In the structure reported here, the carbonyl group of the ester is, as expected, almost coplanar with the phenyl ring of the terephthalate. The conformation of the aliphatic chain is not fully *trans*-planar; there is a *gauche* bond. Molecules are stacked in layers with a herring-bone type of packing within the layers.

Comment

Terephthalic and *p*-hydroxybenzoic acids are among the most widely used groups for the synthesis of both monomers and polymers which form liquid crystals. Condensation of these groups with various *p,p'*-difunctionalized aromatic compounds leads to linear high axial ratio structures (esters, amides, *etc.*) which favor the formation of liquid-crystal phases (Ober, Jin & Lenz, 1984). In previously reported structures of esters of terephthalic, *p*-hydroxybenzoic and related aromatic carboxylic acids (Schweizer & Dunitz, 1982; Centore *et al.*, 1991), the carbonyl group of the ester is found to be coplanar or almost coplanar with the phenyl ring to which it is attached. Consistent with this, semi-empirical quantum-mechanical calculations for 'gas-phase' phenyl benzoate (Bicerano & Clark, 1988) indicate an energy about 6.7 kcal mol^{-1} greater for the 'perpendicular' arrangement of carbonyl group and phenyl ring, compared with the lowest energy coplanar conformation. Deviations from the coplanar arrangement are only observed as a result of great overcrowding, *e.g.* in the crystal structures of 2,6-disubstituted benzoic acids (Anca, Martinez-Carrera & Garcia-Blanco, 1967; Florencio & Smith, 1970). On the basis of solid-state CP/MAS NMR analysis on crystals of the title compound, (I), Uryu & Kato (1988) reported that the carbonyl group of the ester is almost perpendicular to the plane of the terephthalate phenyl ring. They also reported that the planes of the three phenyl rings of the molecule were parallel, which is rare in the crystal structures of phenyl esters of aromatic acids, and that the aliphatic chains were planar zigzag. We undertook the crystal structure determination reported here in order to establish definitively the conformation in the solid state.



(I)

The thermal properties of the title compound as prepared by us are consistent with literature data (crystal–nematic transition: T_m = 460.4 K, ΔH_m = 45.8 kJ mol^{-1}; nematic–isotropic transition: T_i = 505.0 K, ΔH_i = 0.45 kJ mol^{-1}). Particular care was taken to detect possible solid-state polymorphs; samples recrystallized from ethyl acetate [as reported by Uryu & Kato (1988)] and from various other solvents or solvent mixtures (chloroform–ethanol, chloroform–*n*-hexane, toluene) all have identical DSC thermograms.

The molecules in the crystals are centrosymmetric and belong to point group $\bar{1}$ (C_i). Bond lengths and angles have normal values. The conformation of the molecule, however, is considerably different from that proposed by Uryu & Kato (1988). The carbonyl group of the ester is almost coplanar with the phenyl ring of the terephthalate [O3—C11—C12—C13 −176.3 (2)°], as is usual in terephthalate esters. The dihedral angle between the planes of the two phenyl rings, C5–C10 and C12–C14, is 65.06 (5)° and is mainly due to the torsion angle around the O2—C8 bond. Furthermore, the conformation of the aliphatic chain is not fully *trans*-planar, a *gauche* conformation being observed around the C3—C4 bond.

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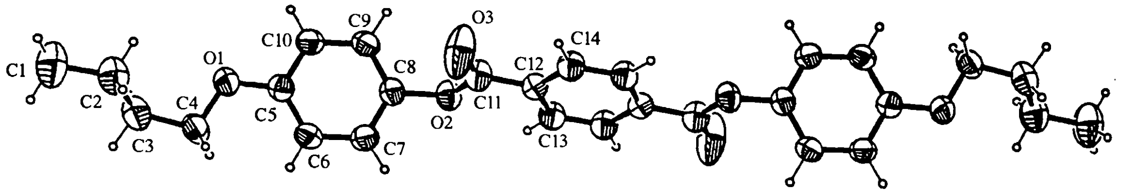

Fig. 1. A view of the molecule showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

The molecules are packed in layers parallel to (100) and stacked along a in a smectic-like fashion. Within each layer, a herring-bone-type packing of the aromatic cores is present, with face-to-edge interactions among the phenyl rings; the packing is similar to that of bis[(4-valeroyloxy)phenyl] terephthalate previously reported by us (Centore *et al.*, 1991). This packing is consistent with theoretical rules proposed by Desiraju & Gavezzotti (1989).

Experimental

The title compound was prepared by straightforward esterification of commercial terephthaloyl chloride and 4-butoxyphenol in dry pyridine at ambient temperature. The raw product obtained from the reaction mixture, after addition of an excess of ethanol and filtration, was purified by column chromatography (silica gel using chloroform as eluent). The final recrystallization was from a chloroform–ethanol mixture.

Crystal data

$C_{28}H_{30}O_6$
$M_r = 462.541$
Monoclinic
$P2_1/c$
$a = 28.019\ (5)$ Å
$b = 5.432\ (1)$ Å
$c = 8.055\ (5)$ Å
$\beta = 95.37\ (6)°$
$V = 1220.6\ (8)$ Å^3
$Z = 2$
$D_x = 1.258$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 24 reflections
$\theta = 13.8$–$19.7°$
$\mu = 0.715$ mm^{-1}
$T = 295$ K
Plate
$0.80 \times 0.80 \times 0.03$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.798$, $T_{\max} = 1.000$
2501 measured reflections
2501 independent reflections

2056 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 75.0°$
$h = 0 \rightarrow 35$
$k = 0 \rightarrow 6$
$l = -10 \rightarrow 10$
1 standard reflection frequency: 120 min
intensity decay: 3.0%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.068$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.267$ e Å^{-3}
$\Delta\rho_{\min} = -0.295$ e Å^{-3}

$S = 1.895$
2056 reflections
214 parameters
All H atoms refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.05F_o^2)^2]$

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C4	1.428 (1)	C5—C10	1.391 (2)
O1—C5	1.373 (1)	C6—C7	1.387 (2)
O2—C8	1.405 (1)	C7—C8	1.372 (2)
O2—C11	1.336 (1)	C8—C9	1.384 (2)
O3—C11	1.192 (2)	C9—C10	1.380 (2)
C1—C2	1.505 (2)	C11—C12	1.484 (2)
C2—C3	1.507 (2)	C12—C13	1.391 (2)
C3—C4	1.509 (2)	C12—C14	1.386 (2)
C5—C6	1.385 (2)	C13—C14^i	1.377 (2)
C4—O1—C5	117.3 (1)	C7—C8—C9	121.6 (1)
C8—O2—C11	118.44 (9)	C8—C9—C10	118.6 (1)
C1—C2—C3	113.6 (2)	C5—C10—C9	120.6 (1)
C2—C3—C4	114.3 (1)	O2—C11—O3	123.0 (1)
O1—C4—C3	107.7 (1)	O2—C11—C12	112.0 (1)
O1—C5—C6	124.1 (1)	O3—C11—C12	125.0 (1)
O1—C5—C10	115.9 (1)	C11—C12—C13	122.3 (1)
C6—C5—C10	120.0 (1)	C11—C12—C14	118.1 (1)
C5—C6—C7	119.5 (1)	C13—C12—C14	119.6 (1)
C6—C7—C8	119.7 (1)	C12—C13—C14^i	119.6 (1)
O2—C8—C7	117.1 (1)	C12—C14—C13^i	120.7 (1)
O2—C8—C9	121.1 (1)		
C5—O1—C4—C3	−179.8 (2)	C1—C2—C3—C4	175.6 (2)
C4—O1—C5—C10	−179.8 (1)	C2—C3—C4—O1	63.3 (2)
C11—O2—C8—C7	112.2 (2)	O2—C11—C12—C14	−178.1 (1)
C8—O2—C11—C12	−175.0 (1)	O3—C11—C12—C13	−176.3 (2)

Symmetry code: (i) $-x, -y, -z$.

Suitable ψ-scan data were not available so *DIFABS* (Walker & Stewart, 1983) was used for the absorption correction, even though this is not entirely appropriate; the U^{ij} values and their s.u.'s may not be dependable.

Data collection: *SDP* (Enraf–Nonius, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1195). Services for accessing these data are described at the back of the journal.

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(Z)-3-Benzylidene-1-ethynyl-1-phenyl-1,3-dihydroisobenzofuran

Reema K. Thalji,[a] Bethzaida Ramos,[b] J. Gabriel Garcia[b] and Frank R. Fronczek[a]

[a]*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA, and* [b]*Clark Atlanta University, Atlanta, GA 30314, USA. E-mail: fronz@chxray1.chem.lsu.edu*

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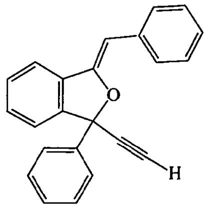
Abstract

The title compound, $C_{23}H_{16}O$, has two independent molecules in the asymmetric unit. The bond lengths and angles of the two molecules are identical. The conformation of the isobenzofuran ring systems of the molecules, however, differ slightly; in molecule *A*, the sp^2-C atom of the five-membered ring deviates the greatest distance [0.034 (2) Å] from the benzo plane, while in molecule *B*, it is the sp^3-C atom of the five-membered ring which has the greatest deviation [0.027 (2) Å] from the benzo plane.

Comment

As part of a structural study involving [3]cumulene intermediates bearing the acetylenic functionality (Ramos & Garcia, 1997), the precursor [1-phenyl-1-(2-phenylethynyl)-3-trimethylsilyl-2-propyn-1-ol] to the title compound was prepared (Ramos & Garcia, 1997). The title compound resulted from an attempt to trimethylsilyl-deprotect the precursor under K_2CO_3 in anhydrous methanol conditions (Austin *et al.*, 1981; Garcia, Ramos, Pratt & Rodriguez, 1995; Garcia, Ramos, Rodriguez & Fronczek, 1995). The title compound, (I), was unexpectedly formed *via* a nucleophilic attack of the hydroxy O atom on the (phenyl)acetylenic functionality, resulting in the formation of the isobenzofuran ring system. Its crystal structure was determined in order to ascertain its identity.



(I)

The title compound exists as two independent molecules in the asymmetric unit, a case which is observed in about 4.6% of compounds having the $P2_1/c$ space group (Brock & Dunitz, 1994). Bond distances and angles of the two molecules are the same within experimental error. The O1*a*—C1*a*, O1*a*—C15*a*, O1*b*—C1*b* and O1*b*—C15*b* bond lengths of 1.385 (2), 1.462 (2), 1.382 (2) and 1.463 (2) Å, respectively, compare well with corresponding lengths in a compound having a similar ring system, *i.e.* 2-isopropyl-4,4,7-trimethyl-1*H*-phenaleno[1,9-*bc*]furan-1-one (Weber *et al.*, 1975). In molecule *A*, the C15 atom lies essentially in the plane of the C9–C14 phenyl ring, deviating from it by only 0.004 (2) Å. The O1*a* and C1*a* atoms, however, deviate by −0.022 (1) and 0.034 (2) Å, respectively, from the same plane. Contrary to C15*a*, C15*b* deviates by −0.027 (2) Å from the plane of the C9–C14 phenyl ring. Atoms O1*b* and C1*b* do not deviate quite as much [0.018 (1) and 0.013 (2) Å, respectively] as C1*a* and O1*a*. Atoms C15*a* and C15*b* lie 0.090 (2) and 0.080 (2) Å out of the C18–C23 phenyl ring planes of their corresponding molecules. The C9*a*—C1*a*—C2*a*—C3*a* torsion angle is 179.5 (2)°, indicating a fairly planar environment about the C1*a*=C2*a* double bond. The C1*b*=C2*b* double bond is less planar, with a C9*b*—C1*b*—C2*b*—C3*b* torsion angle of 178.28 (2)°. The C16*a*≡C17*a* and C16*b*≡C17*b* triple-bond distances of 1.164 (3) and 1.168 (3) Å, respectively, agree with the expected length of 1.174 (4) Å (Allen *et al.*, 1987).