Single-crystal X-ray studies of aromatic oligomers: conformation and packing in oligomeric isophthalate and terephthalate esters

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The structures of diphenyl isophthalate (**1**), bis(4-biphenylyl) isophthalate (**2**), bis(4-benzoyloxyphenyl) isophthalate (**3**) and bis(4-biphenylyl) terephthalate (**4**) have been determined by single-crystal X-ray diffraction. The ester carbonyl groups in (**1**) lie close to the plane of the central isophthalate ring and adopt an *anti* conformation. Crystal packing in (**1**) principally involves carbonyl–carbonyl ($C{=}O^{\delta-}\cdots\cdots{}^{\delta+}C{=}O$) contacts and aromatic edge-to-face ($H\cdots\cdots C$) and face-to-face interactions. Both (**2**) and (**3**) adopt more extended conformations in which the isophthalate carbonyl groups are in the *syn* orientation, and in (**2**) an *anti* arrangement of ester groups about the hydroquinone residue is observed. Compound (**4**) has crystallographic C_i symmetry, within which the central terephthalate ring is inclined at some 61° to near-coplanar biphenyl units. The intermolecular contacts in (**2**), (**3**) and (**4**) are dominated by aromatic edge-to-face interactions and result in non-overlapping, lamella-type crystal packing for these three oligomers.

(Keywords: oligomer; crystal structure; isophthalate; terephthalate; X-ray)

INTRODUCTION

High-performance thermoplastics based exclusively on aromatic structures are rapidly increasing in technological importance as a result of their unique combination of toughness, lightness, dimensional stability at high temperatures and resistance to thermo-oxidative degradation. Although amorphous polymers of this type (poly(ether sulphone)[1] and poly(ether imide)[2] for example) offer relative ease of synthesis and processing, semicrystalline materials such as the poly(ether ketones)[3] can provide additional advantages of enhanced stiffness, temperature performance and resistance to solvent attack. In addition, *liquid*-crystalline aromatic polymers (particularly the lyotropic polyamides and thermotropic polyesters) allow facile control of molecular order during processing as a result of their extended, essentially linear, chain conformations[4].

In order to develop a more exact understanding of aromatic polymer structures and the factors governing their amorphous, crystallizable, or mesomorphic behaviour, we have undertaken a series of single-crystal X-ray studies of monodisperse aromatic oligomers. These studies are intended to provide a database of accurate conformational and packing information, and should help to establish criteria for predicting aromatic polymer structures from small-molecule data. The actual relationship between oligomer and polymer structure in certain aromatic systems has been a subject of some recent debate[5], and one of the principal objectives of the present work is to determine minimum chain lengths at which the conformational and packing preferences of aromatic oligomers genuinely approach those of the corresponding polymer molecules.

RESULTS AND DISCUSSION

Isophthalic acid and terephthalic acid are important constituents of many aromatic polyesters, including several thermotropic materials[6], yet the conformations of the basic diaryl iso- and terephthalate units are experimentally unknown. Recent quantum-mechanical calculations[7,8] have indicated a number of probable minimum-energy conformations, although no definite conformational preferences were identified for isophthalates and the dependence of conformation on chain length or on packing effects was not investigated. In this paper we report the crystal and molecular structures of a number of oligomeric isophthalate esters, including diphenyl isophthalate (**1**), bis(4-biphenylyl) isophthalate (**2**) and bis(4-benzoyloxyphenyl) isophthalate (**3**), results which establish two preferred conformations for the isophthalate fragment and moreover demonstrate a

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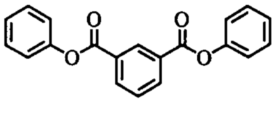
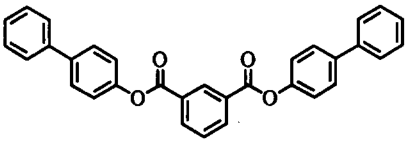
clear-cut relationship between conformation and oligomer chain length. We have also included a study of bis(4-biphenylyl) terephthalate (**4**), in view of its close relationship to a subunit of the thermotropic polymer Xydar* (a copolyester based on terephthalic acid, 4,4'-dihydroxybiphenyl and 4-hydroxybenzoic acid[9]), for which a preliminary X-ray analysis was recently reported[10].



(1)



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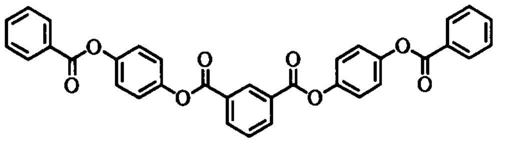

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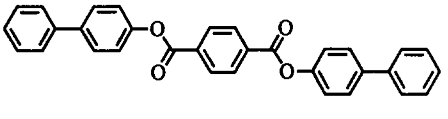

(4)

A perspective view of the diphenyl isophthalate molecule (**1**), with crystallographic numbering, is shown in *Figure 1*. One of the two crystallographically independent molecules of bis(4-biphenylyl) isophthalate (**2**) is shown in *Figure 3*, and the corresponding view of bis(4-benzoyloxyphenyl) isophthalate (**3**) is shown in *Figure 4*. The molecular structure of bis(4-biphenylyl) terephthalate (**4**) is indicated in *Figure 7*. Fractional atomic coordinates for the non-hydrogen atoms of (**1**), (**2**) and (**4**) are given in *Tables 1, 2* and *3* respectively, and selected bond lengths and angles are listed in *Tables 4, 5* and *6*†.

Undoubtedly the most significant feature of structure (**1**) is the *anti* relationship between the two ester carbonyl groups (*Figure 1*). Both ester functions approach coplanarity with the central aromatic ring, although the carbonyl groups C(7)=O(7) and C(14)=O(14) are actually rotated slightly out of this plane, in opposite senses, by some 10° and 7° respectively. The terminal phenyl rings are each rotated by ~66° from coplanarity with their associated ester groups, these rotations being in the *same* sense relative to the central ring. The dihedral angles between the central and outer rings are 55° and 61° for C(1)–C(6) and C(16)–C(21) respectively.

Table 1 Atomic coordinates (× 10^4) and temperature factors (Å^2 × 10^3) for (**1**), with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}^{a}
C(1)	8062(5)	4548(5)	4400(1)	70(1)
C(2)	8814(5)	4994(6)	4778(1)	81(1)
C(3)	7654(7)	6027(6)	5031(1)	83(1)
C(4)	5776(6)	6631(6)	4912(1)	82(1)
C(5)	4998(6)	6214(6)	4532(1)	76(1)
C(6)	6161(5)	5166(4)	4284(1)	59(1)
O(6)	5525(4)	4772(4)	3884(1)	74(1)
C(7)	3837(5)	3755(5)	3831(1)	58(1)
O(7)	2850(4)	3183(5)	4107(1)	87(1)
C(8)	3394(4)	3427(4)	3398(1)	52(1)
C(9)	1553(4)	2592(5)	3297(1)	65(1)
C(10)	1114(4)	2185(5)	2902(1)	74(1)
C(11)	2516(4)	2588(5)	2599(1)	64(1)
C(12)	4351(4)	3426(4)	2692(1)	51(1)
C(13)	4787(4)	3850(4)	3093(1)	50(1)
C(14)	5904(4)	3874(4)	2378(1)	56(1)
O(14)	7421(3)	4719(4)	2443(1)	77(1)
O(15)	5421(3)	3211(3)	2009(1)	65(1)
C(16)	6820(5)	3476(5)	1689(1)	60(1)
C(17)	6218(7)	4448(5)	1364(1)	78(1)
C(18)	7595(9)	4630(6)	1037(1)	97(2)
C(19)	9449(8)	3814(6)	1045(1)	97(2)
C(20)	10041(6)	2831(6)	1371(1)	89(1)
C(21)	8720(5)	2649(5)	1696(1)	71(1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor

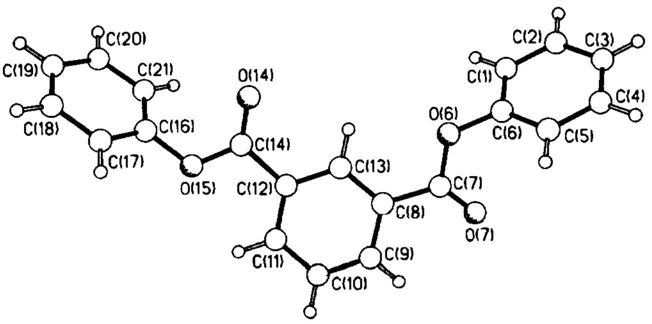

Figure 1 The molecular structure of diphenyl isophthalate (**1**)

The gross molecular conformation of (**1**) approximates to one of the minimum-energy structures recently predicted on quantum-mechanical grounds[8], but there are also a number of important differences. The isophthalate carbonyl groups were for example predicted to be exactly coplanar with the central ring, whereas 7° and 10° rotations are in fact observed; also the torsion angles between the ester and terminal phenyl groups were predicted to be 44° in opposite senses, rather than the observed 66° in the same sense. The experimental values are, however, in close agreement with figures for the corresponding torsion angles in the crystal structure of phenyl benzoate (9.6° and 67.2° respectively)[11].

A stereoscopic view of the molecular packing of (**1**) is shown in *Figure 2*. Molecules are aligned with their long axes approximately in the crystallographic *c* direction, with significant overlap occurring between the terminal rings of adjacently stacked molecules. The principal intermolecular contacts can be summarized as (a) carbonyl-oxygen to carbonyl-carbon ($O^{\delta-} \cdots\cdots C^{\delta+} = 3.38$ Å), (b) aromatic edge-to-face interactions (minimum centroid–centroid distance 5.09 Å) and (c) aromatic face-to-face contacts (minimum centroid–centroid distance 4.17Å, interplanar separation 3.65 Å). It should be noted that the latter two types of contact correspond very closely to the respective global and local potential-energy

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* 'Xydar' is a trademark of the Amoco Corporation

† In view of the relatively poor crystal quality and consequently high *R* factor (0.170) for the structure of oligomer (**3**), detailed geometric parameters are not given, but are available from the authors on request

Table 2 Atomic coordinates (× 10^4) and temperature factors (Å^2 × 10^3) for (**2**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{eq} [a]
C(1)	7270(11)	−2777(13)	2031(1)	56(1)
C(2)	7939(12)	−1425(10)	2230(2)	72(1)
C(3)	8731(11)	577(10)	2167(1)	67(1)
C(4)	8731(10)	1288(11)	1911(1)	66(1)
C(5)	7970(7)	−22(10)	1715(1)	29(1)
C(6)	7124(10)	−1993(13)	1778(1)	50(1)
C(7)	7803(9)	964(9)	1433(1)	48(1)
C(8)	8634(10)	2952(9)	1369(1)	59(1)
C(9)	8661(9)	3750(11)	1116(1)	48(1)
C(10)	7704(8)	2507(8)	934(1)	39(1)
C(11)	6840(9)	522(9)	982(1)	45(1)
C(12)	6973(9)	−255(10)	1235(1)	35(1)
O(13)	7522(7)	3438(9)	687(1)	52(1)
C(14)	8053(8)	2361(11)	484(1)	30(1)
O(14)	8728(10)	543(12)	497(1)	85(1)
C(15)	7692(8)	3644(11)	242(1)	36(1)
C(16)	7069(10)	5818(13)	247(2)	49(1)
C(17)	6780(10)	6853(12)	10(1)	47(1)
C(18)	6980(10)	5786(11)	−227(1)	46(1)
C(19)	7697(8)	3612(11)	−223(1)	30(1)
C(20)	8094(8)	2530(10)	14(1)	32(1)
C(21)	7952(8)	2402(11)	−479(1)	33(1)
O(21)	8672(8)	637(10)	−490(1)	71(1)
O(22)	7373(5)	3571(8)	−682(1)	34(1)
C(23)	7287(7)	2459(7)	−925(1)	25(1)
C(24)	7949(10)	3862(10)	−1113(1)	57(1)
C(25)	7954(9)	2944(10)	−1360(1)	44(1)
C(26)	7135(8)	932(9)	−1428(1)	30(1)
C(27)	6416(11)	−262(13)	−1227(1)	62(1)
C(28)	6447(9)	425(8)	−970(1)	47(1)
C(29)	7103(8)	20(11)	−1712(1)	33(1)
C(30)	7796(10)	1302(12)	−1910(1)	54(1)
C(31)	7784(11)	544(9)	−2164(1)	74(1)
C(32)	6994(9)	−1515(9)	−2208(1)	59(1)
C(33)	6229(9)	−2823(10)	−2020(1)	56(1)
C(34)	6344(10)	−2035(13)	−1767(1)	49(1)
C(51)	−1177(11)	5044(11)	7018(1)	83(1)
C(52)	−1971(10)	3947(12)	7222(1)	70(1)
C(53)	−2937(11)	2060(12)	7149(1)	65(1)
C(54)	−3011(10)	1284(13)	6895(1)	64(1)
C(55)	−2170(10)	2280(11)	6687(1)	57(1)
C(56)	−1247(11)	4179(12)	6768(1)	65(1)
C(57)	−2248(9)	1517(12)	6435(1)	55(1)
C(58)	−3143(11)	−456(12)	6373(2)	64(1)
C(59)	−3193(9)	−1190(12)	6119(1)	43(1)
C(60)	−2277(12)	−218(15)	5927(2)	72(1)
C(61)	−1375(11)	1645(12)	5994(1)	69(1)
C(62)	−1375(9)	2627(11)	6239(1)	54(1)
O(63)	−1991(7)	−1031(10)	5677(1)	60(1)
C(64)	−2930(10)	3(13)	5460(1)	65(1)
O(64)	−3666(8)	1790(11)	5492(1)	63(1)
C(65)	−2629(10)	−1274(12)	5240(1)	56(1)
C(66)	−1967(11)	−3318(15)	5230(2)	48(1)
C(67)	−1552(10)	−4369(13)	4998(2)	54(1)
C(68)	−2064(10)	−3309(12)	4768(1)	48(1)
C(69)	−2875(9)	−1180(12)	4771(1)	46(1)
C(70)	−3174(9)	−256(14)	5014(1)	54(1)
C(71)	−3372(11)	87(15)	4524(2)	64(1)
O(71)	−3995(7)	1766(9)	4504(1)	52(1)
O(72)	−2549(7)	−1104(10)	4314(1)	54(1)
C(73)	−2728(10)	−101(9)	4068(1)	62(1)
C(74)	−3564(10)	−1267(12)	3866(1)	63(1)
C(75)	−3705(10)	−409(13)	3616(1)	48(1)
C(76)	−2889(9)	1505(11)	3546(1)	37(1)
C(77)	−1907(13)	2627(16)	3740(1)	75(1)
C(78)	−1947(11)	1889(9)	3996(1)	64(1)
C(79)	−2780(9)	2213(8)	3286(1)	61(1)
C(80)	−3669(9)	1100(11)	3083(1)	53(1)
C(81)	−3675(12)	1861(10)	2827(1)	64(1)
C(82)	−2899(11)	3892(10)	2770(2)	62(1)
C(83)	−1936(11)	5054(14)	2963(1)	73(1)
C(84)	−2109(11)	4281(9)	3215(1)	66(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 3 Atomic coordinates (× 10^4) and temperature factors (Å^2 × 10^3) for (**4**), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{eq} [a]
C(1)	7603(3)	6770(5)	3650(1)	51(1)
C(2)	7322(4)	6767(6)	4159(1)	58(1)
C(3)	8008(3)	4988(6)	4482(1)	54(1)
C(4)	8950(4)	3219(6)	4290(1)	59(1)
C(5)	9220(4)	3215(5)	3778(1)	52(1)
C(6)	8571(3)	5008(4)	3446(1)	36(1)
C(7)	8886(3)	5048(4)	2896(1)	36(1)
C(8)	9833(3)	3276(5)	2685(1)	45(1)
C(9)	10137(3)	3336(5)	2178(1)	47(1)
C(10)	9513(3)	5194(5)	1874(1)	40(1)
C(11)	8571(4)	6996(5)	2066(1)	51(1)
C(12)	8272(3)	6915(5)	2572(1)	50(1)
O(13)	9883(2)	5462(3)	1368(1)	48(1)
C(14)	9279(3)	3819(5)	1015(1)	50(1)
O(14)	8499(4)	2093(5)	1119(1)	101(1)
C(15)	9682(3)	4472(5)	496(1)	41(1)
C(16)	10538(3)	6549(5)	396(1)	47(1)
C(17)	9143(3)	2924(5)	95(1)	46(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4 Selected bond lengths (Å) and angles (deg) for (**1**) with estimated standard deviations in parentheses

C(6)–O(6)	1.408(3)	O(6)–C(7)	1.352(4)
C(7)–O(7)	1.191(4)	C(7)–C(8)	1.474(4)
C(12)–C(14)	1.480(4)	C(14)–O(14)	1.194(4)
C(14)–O(15)	1.352(3)	O(15)–C(16)	1.402(4)
C(6)–O(6)–C(7)	118.6(2)	O(6)–C(7)–O(7)	123.1(3)
O(6)–C(7)–C(8)	112.3(2)	O(7)–C(7)–C(8)	124.6(3)
C(7)–C(8)–C(9)	118.3(3)	C(7)–C(8)–C(13)	122.3(3)
C(13)–C(12)–C(14)	118.1(2)	C(11)–C(12)–C(14)	122.3(2)
C(12)–C(14)–O(14)	123.9(3)	C(12)–C(14)–O(15)	112.5(2)
O(14)–C(14)–O(15)	123.5(3)	C(14)–O(15)–C(16)	118.1(2)

Table 5 Selected bond lengths (Å) and angles (deg) for one of the two independent molecules of (**2**) with estimated standard deviations in parentheses

C(5)–C(7)	1.569(7)	C(10)–O(13)	1.393(7)
O(13)–C(14)	1.306(8)	C(14)–O(14)	1.206(9)
C(14)–C(15)	1.485(8)	C(19)–C(21)	1.530(9)
C(21)–O(21)	1.193(9)	C(21)–O(22)	1.324(7)
O(22)–C(23)	1.418(6)	C(26)–C(29)	1.562(8)
C(10)–O(13)–C(14)	120.8(5)	O(13)–C(14)–O(14)	122.8(6)
O(13)–C(14)–C(15)	111.4(5)	O(14)–C(14)–C(15)	125.8(6)
C(19)–C(21)–O(21)	122.2(6)	C(19)–C(21)–O(22)	112.7(6)
O(21)–C(21)–O(22)	125.0(6)	C(21)–O(22)–C(23)	116.9(5)

Table 6 Selected bond lengths (Å) and angles (deg) for (**4**) with estimated standard deviations in parentheses

C(6)–C(7)	1.497(3)	C(10)–O(13)	1.402(3)
O(13)–C(14)	1.353(3)	C(14)–O(14)	1.193(4)
C(14)–C(15)	1.480(4)		
C(10)–O(13)–C(14)	118.9(2)	O(13)–C(14)–O(14)	122.7(2)
O(13)–C(14)–C(15)	111.6(2)	O(14)–C(14)–C(15)	125.6(3)

minima identified theoretically for two interacting aromatic rings[12,13].

The most striking feature of structures (**2**) and (**3**) (*Figures 3* and *4*), when compared with the *anti* structure of diphenyl isophthalate, is the *syn* conformation of the isophthalate unit. This results from an approximately 180° rotation of one of the ester groups from its position in diphenyl isophthalate, and leads to local, non-crystallographic C_s symmetry for both of the five-ring isophthalates.

In the structure of (**2**) the isophthalate carbonyl groups are rotated only very slightly out of the plane of the central ring, by between 1° and 7° (in the same sense) in both independent molecules (*Figure 3*). The biphenyl units are essentially planar with inter-ring dihedral angles of $<4°$, and the 'phenolic' rings of these units are rotated by between 47° and 76°, in the same sense, relative to their associated ester functions. The dihedral angles between the central isophthalate ring and adjacent rings fall in the range 49–60°.

In the two independent molecules of structure (**3**) there is a much greater spread of values (5–24°) for rotation of the isophthalate carbonyl groups out of the plane of the central ring than is found in (**2**) (*Figure 4*). The sequence of inter-ring dihedral angles, however, remains in a similar range (51–60°) to that observed for the ester-linked rings in structure (**2**). Overall, the molecule (**3**) has an almost fully extended conformation, with the ester groups adopting an *anti* orientation about the hydroquinone residues. Together with the *syn* conformation of the isophthalate unit, this leads to near-coplanarity of *alternate* rings along the oligomer chain.

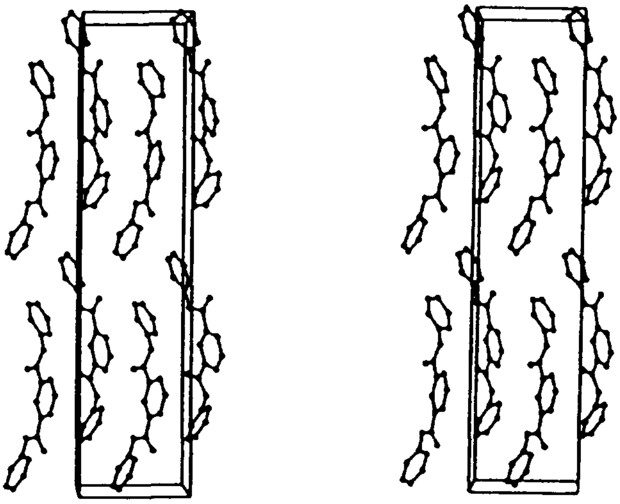
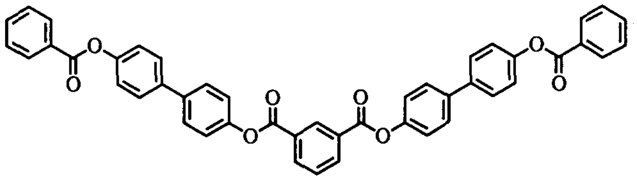


Figure 2 Stereoscopic view of the molecular packing in (**1**)

A second notable difference between the crystal structures of (**2**) and (**3**) and that of diphenyl isophthalate (**1**) is the occurrence in both the five-ring compounds of non-overlapping, lamella-type packing (*Figure 5*). Viewed along the chain axes, both structures (**2**) and (**3**) display polymer-like near-hexagonal packing, with a slight flattening in the *a* direction (*Figure 6*). The dominant packing interactions in both (**2**) and (**3**) are aromatic edge-to-face (H·····C) contacts (ring centroid–centroid distances averaging 4.7 Å; interplanar angles 42–66°), which exist for all five rings in both structures. Ester–ester contacts are also present, however, with carbonyl oxygens almost equidistant from carbonyl carbons (2.97–3.15 Å) and 'phenolic' oxygens (3.02–3.34 Å) of adjacently stacked molecules.

The seven-ring oligomer bis(4-benzoyloxybiphenyl) isophthalate (**5**) was also synthesized in the course of this work, but we have not yet been able to grow single crystals suitable for X-ray analysis. Powder diffraction patterns for (**3**) and (**5**) in the mid- to high-angle region are, however, very closely correlated (*Table 7*), and even at low angles the only significant differences are, as might be expected, in the series of 00*l* lines, which reflect the oligomer chain length and inter-lamella spacing. A lamella thickness of ~38 Å is thus obtained for oligomer (**5**), in excellent agreement with a theoretical value of 38.0 Å calculated using a combination of data from structures (**2**) and (**3**), assuming *syn* geometry at isophthalate and an *anti* arrangement of ester groups about biphenyl.



(**5**)

Recent polymer diffraction studies have indicated the crystallographic fibre repeat of poly(1,4-phenylene isophthalate) to be ~24.3 Å, a figure which it was suggested

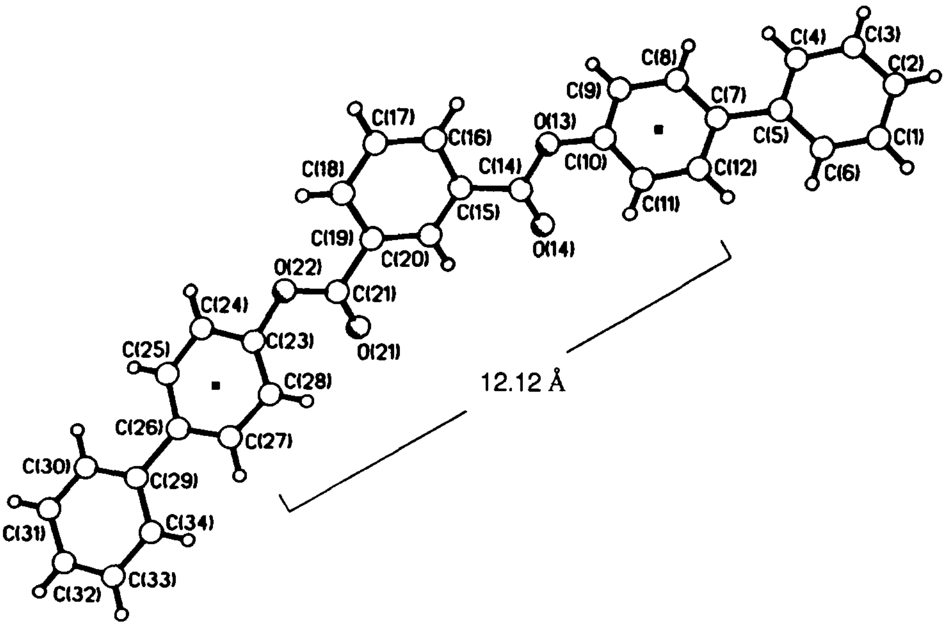


Figure 3 The molecular structure of bis(4-biphenylyl) isophthalate (**2**), showing atom numbering and intramolecular ring centroid–centroid distances

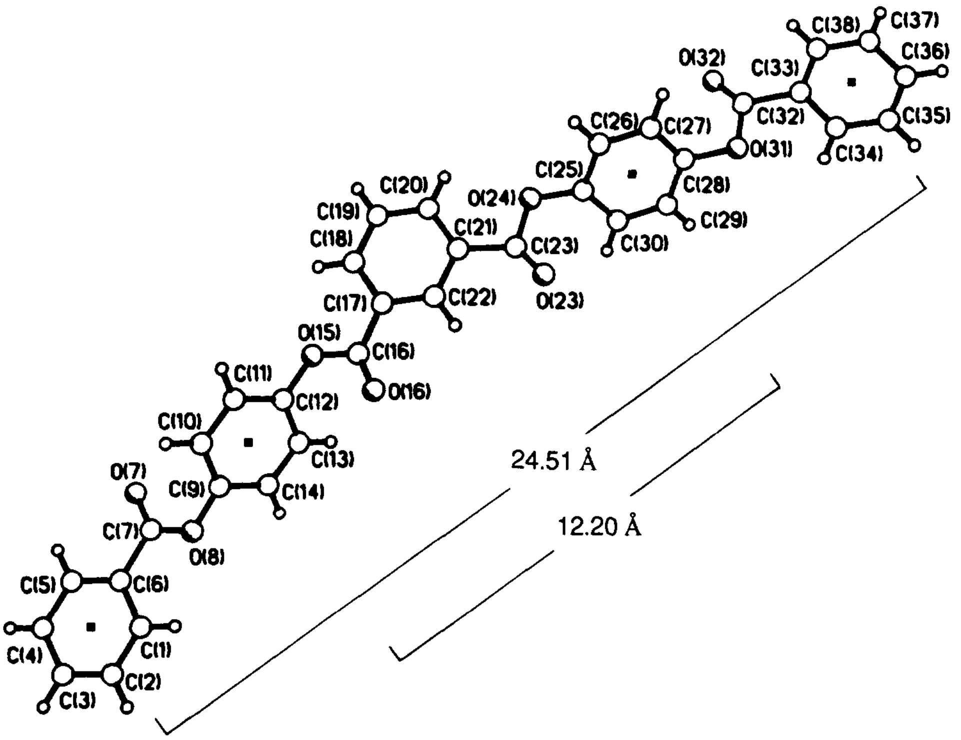


Figure 4 The molecular structure of bis(4-benzoyloxyphenyl) isophthalate (3), showing atom numbering and intramolecular ring centroid–centroid distances

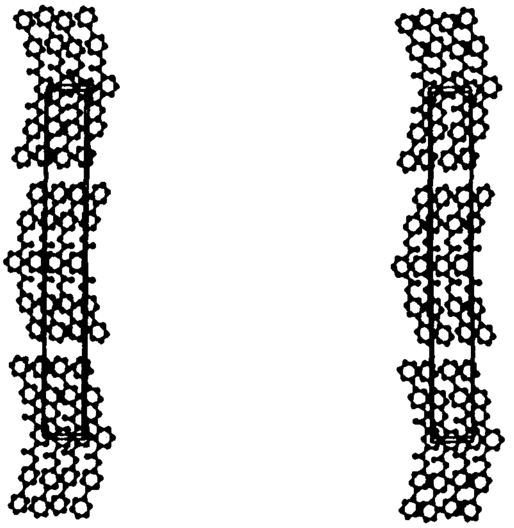


Figure 5 Stereoscopic view of the molecular packing in (2)

Table 7 Principal features of the X-ray powder patterns for (3) and (5)[a]

Compound (3)		Compound (5)	
d spacing (Å)	Intensity	*d* spacing (Å)	Intensity
1.78	w	1.79	w
1.82	w	1.83	w
1.91	m, br	1.91	m, br
2.30	s, br	2.30	s, br
3.05	m	3.05	s
3.13	vs	3.15	vs
3.75	vs, br	3.75	vs, br
4.45–4.63	vs, br	4.40–4.62	vs, vbr
10.0	w	12.8	w
15.0	w	19.0	w

[a] Diffraction peaks in last two lines are chain-length-dependent (0 0 *l*)-type reflections

requires a 25° rotation of the ester carbonyl groups from the plane of the isophthalate ring in order to reduce the repeat distance from a calculated 'planar' value of 24.56 Å[14]. Values obtained from ring centroid–centroid distances in the present oligomer structures (*Figure 3*), however, show that the *shortest* repeat ($2 \times 12.12 = 24.24$ Å) is associated with the *smallest* rotations of isophthalate carbonyl groups from the plane of the central ring (5° and 7°). This result indicates that large distortions from coplanarity are *not* required to account for the crystallographic repeat observed in poly(1,4-phenylene isophthalate). Conversely, the fact that good agreement is observed between oligomer and polymer data strongly suggests that the essential conformational features of poly(arylene isophthalates) are genuinely represented in structures (**2**) and (**3**).

In agreement with recent theoretical studies of the diaryl terephthalate unit[7], which suggested a minimum-energy conformation in which the ester groups are coplanar and adopt the *anti* conformation, structure (**4**) reveals a molecule with crystallographic C_i symmetry (*Figure 7*). The ester carbonyl groups are thus indeed *anti*, and are twisted out of the plane of the central ring by little more than 2°. (The corresponding torsion angles in dimethyl and diethyl terephthalate are 4.7° and 0.8° respectively[15,16].) The biphenyl units are very nearly planar, with an inter-ring dihedral angle of only 1.6°, and the 'phenolic' rings of these units are inclined to the plane of the central ring at an angle of ~61°.

As in the corresponding isophthalate ester (**2**) the molecules of (**4**) pack in non-overlapping lamellar fashion, with their long axes oriented at ~7° to the crystallographic *c* direction (*Figure 8*). Intermolecular contacts are again dominated by aromatic edge-to-face interactions (ring centroid–centroid distances averaging 4.86 Å, at an inter-ring angle of ~63°) and by ester–ester

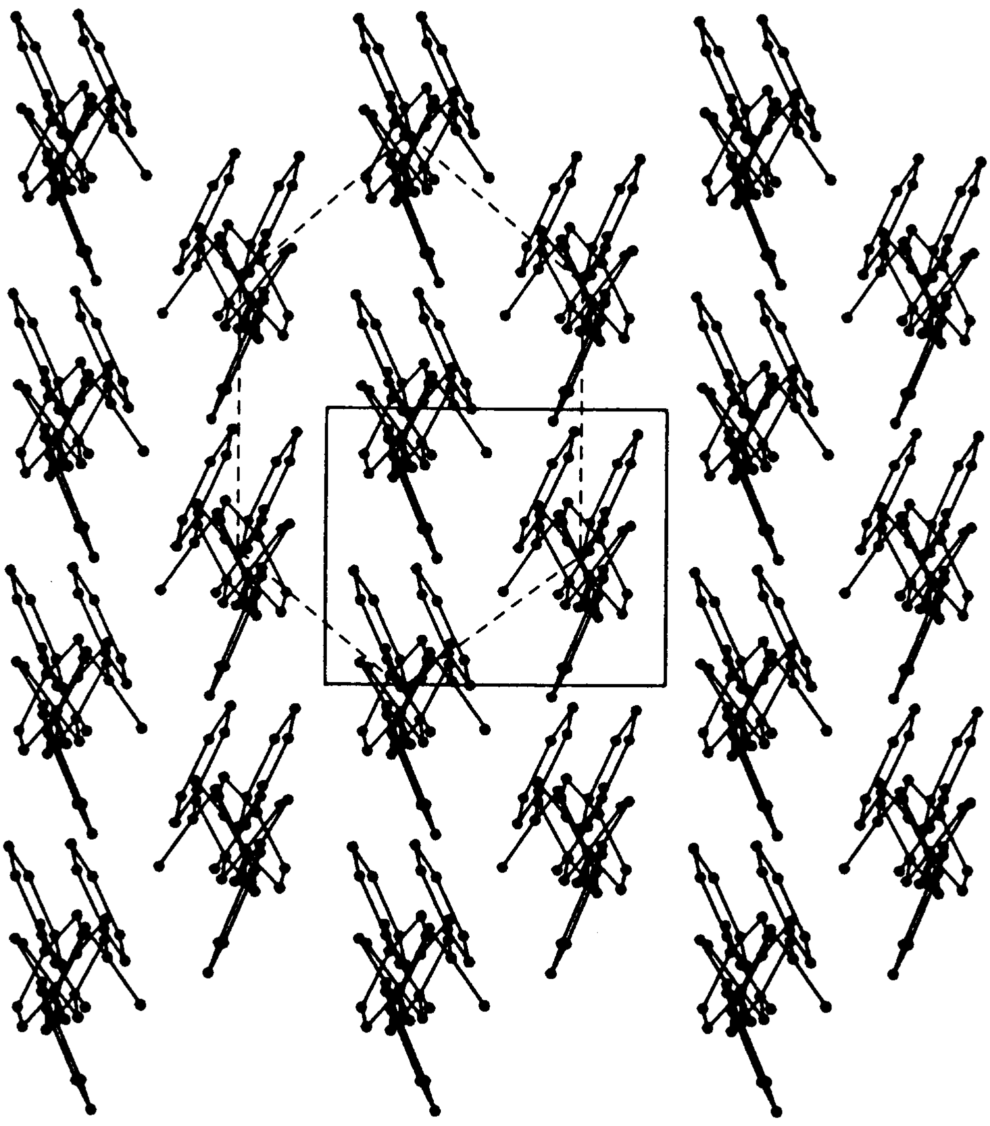


Figure 6 Flattened hexagonal packing array of molecules of (3), viewed along the crystallographic *c* direction

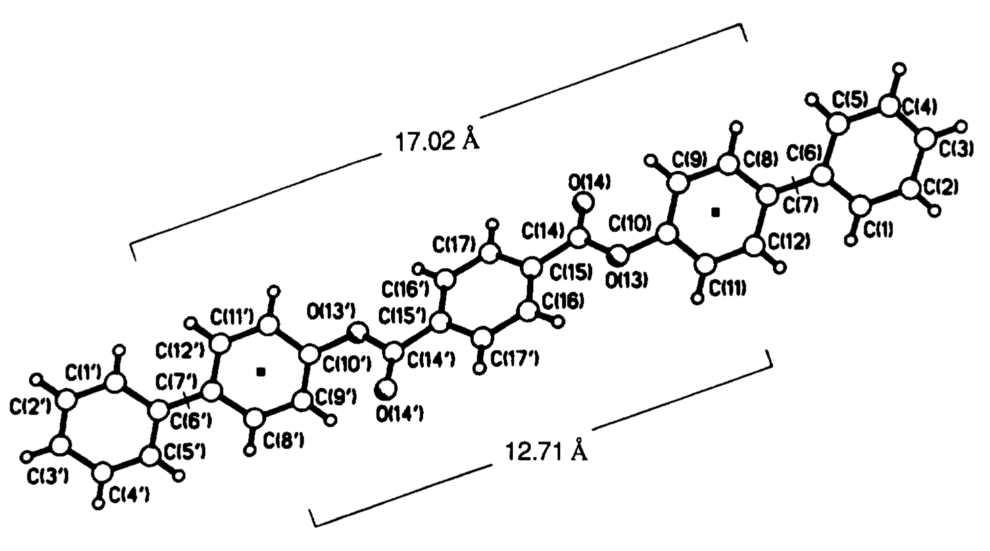


Figure 7 The molecular structure of bis(4-biphenylyl) terephthalate (4), showing phenylene terephthalate and biphenylene terephthalate unit dimensions. Distances are between ring centroids or bond centres

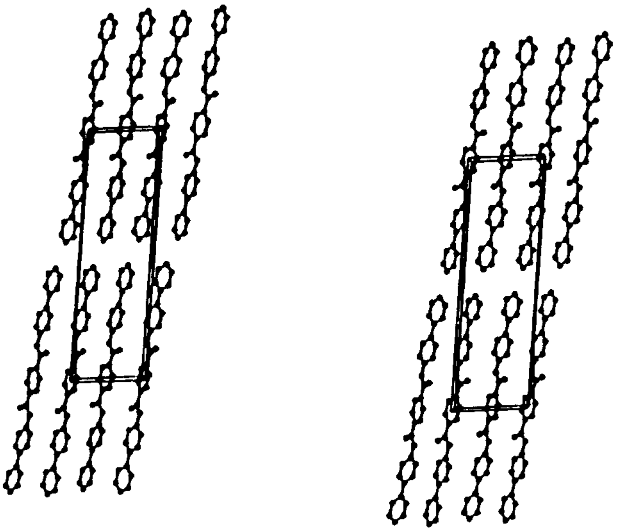


Figure 8 Stereoscopic view of the crystal packing in (**4**)

contacts (O=C·····O=C at ~3.35 Å, C=O·····O—C=O at ~3.32 Å).

This structure is of particular relevance to a recent X-ray study of the copolyester Xydar[10], a material that contains an appreciable fraction of the bis(4-biphenylyl) terephthalate subunit. In this study it was assumed that the torsion angles between phenylene and ester groups are randomly ±30°, which while allowing ester-linked rings to be inclined at 60°, as found here, also suggests that such pairs of rings could equally well be *parallel*. Since there is, in all the aromatic ester structures we have so far examined, a marked tendency for the ester carbonyl group to lie within a few degrees of the plane of its attached aromatic ring, and for the ring attached to 'phenolic' oxygen to rotate from the plane of the ester group by some 60–70°, the occurrence of parallel ester-linked aromatic rings seems improbable, at least in polyesters derived from dicarboxylic acids*.

EXPERIMENTAL

Materials

Compounds (**1**), (**2**), (**3**) and (**5**) were obtained by reaction of isophthaloyl chloride in pyridine with 2.1 mol of phenol, 4-phenylphenol, 4-benzoyloxyphenol and 4-(4-benzoyloxyphenyl)phenol respectively. After stirring for 4 h at room temperature the products were precipitated by pouring into excess 2 M hydrochloric acid, filtered off and recrystallized from appropriate solvents. Compound (**4**) was similarly obtained from 4-phenylphenol and terephthaloyl chloride. Single crystals suitable for X-ray analysis were grown by slow evaporation of solutions in dichloromethane–methanol (for (**1**) and (**3**)), dichloromethane–acetonitrile (for (**2**)) or dichloromethane–trifluoroacetic acid (for (**4**)).

Crystal data

Compound (**1**). $C_{20}H_{14}O_4$, $M=318.3$, orthorhombic, $a=6.463(2)$, $b=7.658(2)$, $c=32.870(9)$ Å, $U=1626$ Å^3, space group $Pc2_1b$, $Z=4$, $D_c=1.30\,\mathrm{g\,cm^{-3}}$, Cu K$_\alpha$ radiation, $\mu(\mathrm{Cu\,K_\alpha})=7\,\mathrm{cm^{-1}}$, $F(000)=663$.

Compound (**2**). $C_{32}H_{22}O_4$, $M=470.5$, monoclinic, $a=7.503(1)$, $b=6.015(1)$, $c=51.619(11)$ Å, $\beta=91.87(2)°$, $U=2329$ Å^3, space group $P2_1$, $Z=4$ (two crystallographically independent molecules), $D_c=1.34\,\mathrm{g\,cm^{-3}}$, Cu K$_\alpha$ radiation, $\mu(\mathrm{Cu\,K_\alpha})=7\,\mathrm{cm^{-1}}$, $F(000)=984$.

Compound (**3**). $C_{34}H_{22}O_8$, $M=558.5$, monoclinic, $a=7.508(3)$, $b=5.924(3)$, $c=60.664(31)$ Å, $\beta=93.05(4)°$, $U=2693$ Å^3, space group $P2_1$, $Z=4$ (two crystallographically independent molecules), $D_c=1.38\,\mathrm{g\,cm^{-3}}$, Cu K$_\alpha$ radiation, $\mu(\mathrm{Cu\,K_\alpha})=8\,\mathrm{cm^{-1}}$, $F(000)=1160$.

Compound (**4**). $C_{32}H_{22}O_4$, $M=470.5$, monoclinic, space group $P2_1/a$, $a=7.892(2)$, $b=5.585(1)$, $c=26.288(7)$ Å, $\beta=96.57(2)°$, $U=1151$ Å^3, $Z=2$ (centrosymmetric molecule), $D_c=1.36\,\mathrm{g\,cm^{-3}}$, Cu K$_\alpha$ radiation, $\mu(\mathrm{Cu\,K_\alpha})=7\,\mathrm{cm^{-1}}$, $F(000)=492$.

Methods

Data for all four structures were measured using copper K$_\alpha$ radiation (graphite monochromator, $\lambda=1.541\,78$ Å) on a computer-controlled Nicolet R3m diffractometer using ω scans, and of the 1189 independent reflections ($2\theta<116°$) for (**1**), 3522 ($2\theta<116°$) (**2**), 3456 ($2\theta<110°$) for (**3**) and 1553 ($2\theta<116°$) for (**4**), 1120, 2504, 2416 and 1416 respectively had $|F_0|>3\sigma(|F_0|)$ and were considered to be observed. Data were corrected for Lorentz and polarization factors. No absorption corrections were applied.

The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized (C–H = 0.96 Å) and allowed to ride on their parent carbons. Refinement by block-cascade, full-matrix least-squares gave: for (**1**), $R=0.040$, $R_w=0.044$ ($w^{-1}=\sigma^2(F)+0.000\,84F^2$); for (**2**), $R=0.081$, $R_w=0.080$ ($w^{-1}=\sigma^2(F)+0.000\,30F^2$); for (**3**), $R=0.170$, $R_w=0.168$ ($w^{-1}=\sigma^2(F)+0.000\,50F^2$); and for (**4**), $R=0.067$, $R_w=0.079$ ($w^{-1}=\sigma^2(F)+0.000\,50F^2$). Computations were carried out on an Eclipse S140 computer using the SHELXTL program system[18].

X-ray powder patterns were recorded with a Guinier focusing camera using Cu K$_\alpha$ radiation.

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* A parallel-ring conformation has also been proposed for the homopolyester of 4-hydroxybenzoic acid[17], but we have so far been unable to grow diffraction-quality single crystals of the corresponding oligomers

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