Single crystal X-ray studies of aromatic oligomers: structural models for polyimides derived from hexafluoroisopropylidene- and sulfone-bridged dianhydrides

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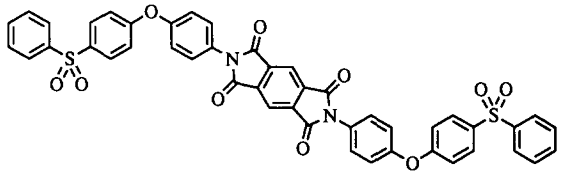
The crystal and molecular structures of two oligomeric aromatic ether-imides PhOArN(OC)$_2$Ar'-X-Ar'(CO)$_2$NArOPh [X = -SO$_2$- (**4**) or -C(CF$_3$)$_2$- (**5**); Ar = a 1,4- and Ar' = a 1,3,4-substituted aromatic residue] have been determined by single crystal X-ray diffraction. Crystal data for **4**, $C_{40}H_{24}N_2O_8S.0.25\,H_2O$: orthorhombic, *Pbnm*; $a = 5.628(1)$, $b = 24.903(8)$, $c = 47.175(17)$ Å. Crystal data for **5**, $C_{43}H_{24}F_6N_2O_6$: monoclinic, $P2_1/c$; $a = 6.919(1)$, $b = 11.977(2)$, $c = 43.203(9)$ Å; $\beta = 94.23(2)°$. Molecules of the sulfone-bridged oligomer **4** pack in discrete chevron-like lamellae, within which complementary, parallel ring-stacking (~ 3.5 Å interplanar separation) occurs between aminophenol (-NC$_6$H$_4$O-) and arene-imide [-Ar(CO)$_2$NAr'-] residues. In contrast, the hexafluoroisopropylidene-bridged oligomer **5** packs in a linearly displaced, non-lamellar fashion in the crystal, the structure showing no evidence for adjacent stacking of electronically complementary molecular sub-units.

(Keywords: X-ray; imide; crystal structure)

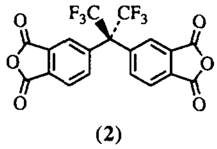
INTRODUCTION

Commercially available aromatic polyimides are currently derived from rigid, linear, dianhydrides, as for example Du Pont's poly(pyromellitimide) Kapton® and the biphenyltetracarboximide-based Upilex® series of resins from Ube. Such materials possess outstanding thermomechanical and oxidative stability[1], but they also have significant limitations in that (1) although processable via their precursor polyamic acids, once imidized they are exceedingly difficult to fabricate‡ and (2) their characteristically intense colours generally rule out optical or opto-electronic applications. These limiting features of polyimide behaviour have often been ascribed, at least in part, to the probable existence of intermolecular charge-transfer interactions between adjacently stacked, electronically complementary regions of the polyimide chains[3]. Direct evidence for this type of complementary stacking has in fact recently been found in the crystal structure of an oligomeric pyromellitimide (1)[4].



(1)

Extensive research has been carried out over the past few years with the aim of reducing colour, increasing solubility, and improving thermoplastic flow in aromatic polyimides[5]. Typical approaches have involved incorporation of sterically bulky units into the chain and the introduction of linking groups with intrinsically non-linear conformations. These structural changes were intended to eliminate or at least reduce charge-transfer between polyimide chains by inhibiting close, parallel, intermolecular ring-stacking, and a particularly successful monomer in this respect has been the hexafluoroisopropylidene-bridged dianhydride '6FDA' (**2**)[6], in which the bridging group is both sterically demanding and inherently non-linear.



(**2**)

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‡ It should be noted however that the polyimide Upilex R, derived from 4,4'-diaminodiphenylether and 3,3',4,4'-biphenyltetracarboxylic dianhydride, can be cast into film from solutions in 1,4-chlorophenol at high temperature[2]

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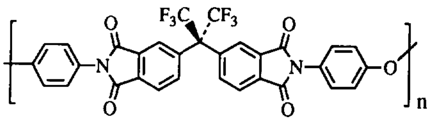
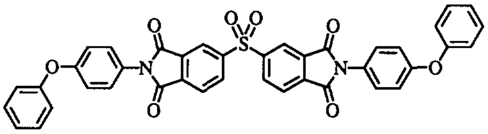
Furthermore, it has recently been shown that, in membrane form, 6FDA-derived polyimides such as **3** possess uniquely high gas permeability and selectivity, e.g. for the separation of methane and carbon dioxide[7]. In contrast, polyimides in which the bridging $-C(CF_3)_2-$ group is replaced by less bulky groups such as $-SO_2-$ give membranes with good selectivity but very much lower permeability[8,9].



(3)

Such variations in polymer properties must obviously result from substantial changes in chain conformation and/or molecular packing, and indeed the membrane characteristics of polymer **3** have been ascribed to a rather open but well-defined helical chain conformation suggested by computer-modelling studies[10]. In order to provide a more quantitative, experimental basis for analysis of such effects, we have carried out a series of single crystal X-ray studies on oligomeric polyimide-analogues, and here report the crystal and molecular structures of the sulfone bridged ether-imide oligomer **4** and its 6FDA-based analogue **5**.



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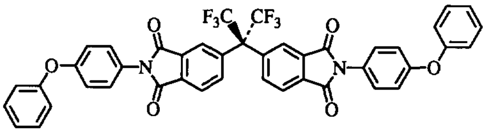

(5)

EXPERIMENTAL

Synthesis and crystallization of oligomers

Oligomer 4. Sulfonyl-di(phthalic anhydride) (8.97 g, 25 mmol) and 4-aminophenyl (phenyl) ether (9.72 g, 52.5 mmol) were added to *N*-methylpyrrolidone (NMP, 50 cm^3) and the mixture was stirred and heated at 160°C for 3 h. After cooling, the resulting slurry was poured into stirred ice/water (250 cm^3) and the precipitate was filtered off, washed with methanol (2 x 50 cm^3) and dried to give a grey powder. The crude yield was 65%, and after two recrystallizations from NMP this material gave pale yellow crystals, m.p. 274–275°C. Single crystals (needles) suitable for X-ray analysis were grown by evaporation from NMP.

Oligomer 5. This compound was prepared as for **4**, but using hexafluoroisopropylidene-di(phthalic anhydride) (6-FDA, 11.11 g, 25 mmol). The crude yield was 58%, and after two recrystallizations from NMP this material gave a pale brown solid, m.p. 244–246°C. Single crystals (plates) suitable for X-ray analysis were grown by evaporation from acetonitrile.

Crystal data

Oligomer 4. $C_{40}H_{24}N_2O_8S.0.25H_2O$, $M=697.2$, orthorhombic, $a=5.628(1)$, $b=24.903(8)$, $c=45.175(17)$ Å, $U=6612$ Å^3, space group $Pbnm$, $Z=8$ (two independent molecules, each with C_s symmetry), $D_c=1.40$ g cm^{-3}, Cu Kα radiation, μ(Cu Kα) = 13 cm^{-1}, F(000) = 2880. Crystal dimensions: 0.83 x 0.07 x 0.07 mm.

Oligomer 5. $C_{43}H_{24}F_6N_2O_6$, $M=778.7$, monoclinic, $a=6.919(1)$, $b=11.977(2)$, $c=43.203(9)$ Å, $\beta=94.23(2)°$, $U=3570$ Å^3, space group $P2_1/c$, $Z=4$, $D_c=1.45$ g cm^{-3}, Cu Kα radiation, μ(Cu Kα) = 10 cm^{-1}, F(000) = 1592. Crystal dimensions: 0.40 x 0.17 x 0.07 mm.

X-ray methods

X-ray data were measured with Cu Kα radiation (graphite monochromator, $\lambda=1.54178$ Å) using ω-scans. Both structures were solved by direct methods and the non-hydrogen atoms refined anisotropically. In oligomer **4** a ΔF map revealed the presence of a partial-weight water molecule ($\sim$0.25 H_2O), and this was refined isotropically. The positions of the hydrogen atoms (other than those of the water molecule) were idealized (C–H = 0.96 Å), assigned isotropic thermal parameters $U(H)=1.2\ U_{eq}(C)$, and allowed to ride on their parent carbons. Refinement was by block-cascade full-matrix least squares to give, for oligomer **4**, $R=0.069$, $R_w=0.061$ $[w^{-1}=\sigma^2(F)+0.00050F^2]$ for 2246 independent observed reflections $[|F_0|>3\sigma(|F_0|), 2\theta\leqslant 110°]$ and for oligomer **5**, $R=0.053$, $R_w=0.051$ $[w^{-1}=\sigma^2(F)+0.00028F^2]$ for 3624 independent observed reflections $[|F_0|>3\sigma(|F_0|), 2\theta\leqslant 116°]$.

Computations were carried out on an Eclipse S140 computer using the SHELXTL program system[11].

RESULTS AND DISCUSSION

The molecular structures of **4** and **5** are shown in *Figures 1* and *2*, and stereoscopic views of the crystal packing observed for these molecules are given in *Figures 3* and *4*. Atomic coordinates are given in *Tables 1* and *2*, and listings of bond lengths, bond angles, and selected torsion angles are given in *Tables 3–8*.

The sulfone-bridged oligomer **4** has crystallographic C_s symmetry, the mirror plane passing through the oxygen and sulfur atoms of the sulfone group. There are two crystallographically independent molecules in the lattice (*Figure 1*), and in each the planar arene-imide residues adopt a conventional 'open-book' conformation about the sulfone bridge. Arene torsion angles relative to the plane of the C–S–C bridge are close to orthogonal in both molecules (C15–C20 at ~91° and C15′–C20′ at ~81°). The aminophenol residues are inclined at ~60° to the planes of their associated imide units, which themselves show no significant out-of-plane distortions.

The terminal diphenyl ether units in oligomer **4** exhibit near-orthogonal relationships between the aromatic rings, a conformation observed previously in the crystal structure of 1,4-diphenoxybenzene[12]. However, in the two independent molecules of oligomer **4**, different overall geometries are observed. The difference (*Figure 1*) involves a ~180° rotation of the terminal rings about O6–C7 and O6a–C7a. The diphenyl ether units in **4** undergo sterically induced in-plane distortions from ideal trigonal geometry at the aromatic ring carbons C7 and C7′. The bond angle O6–C7–C8 for example is appreciably contracted from a standard trigonal value of

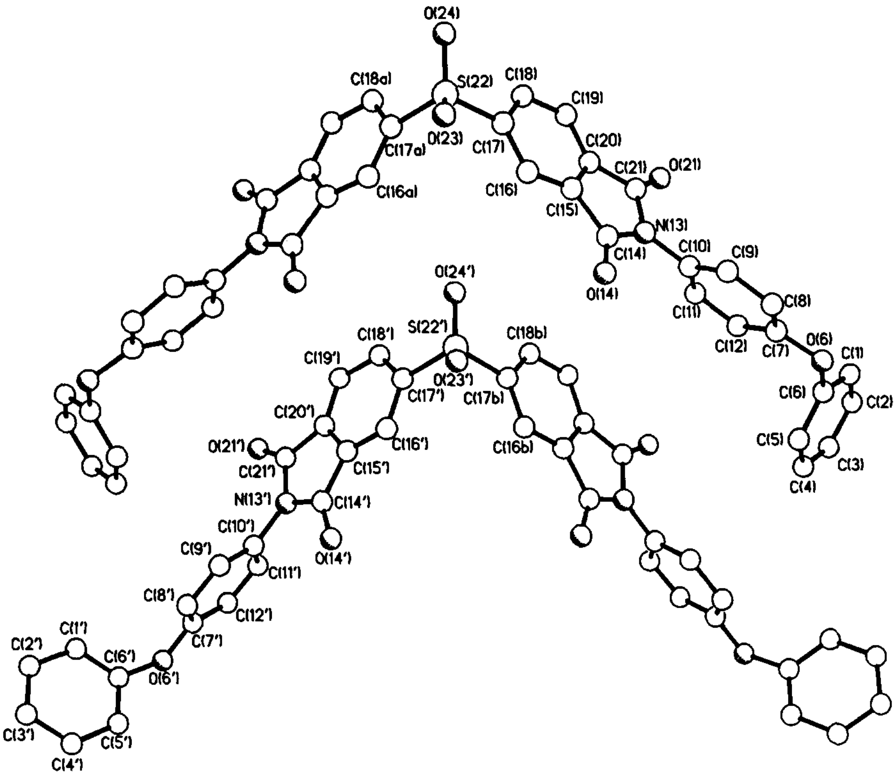

Figure 1 Molecular structure of oligomer **4** (two independent molecules)

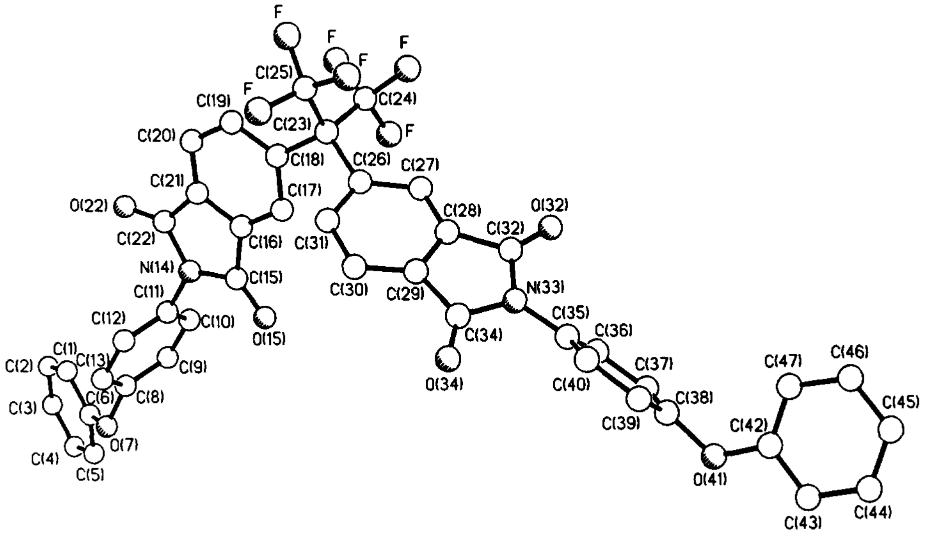

Figure 2 Molecular structure of oligomer **5**

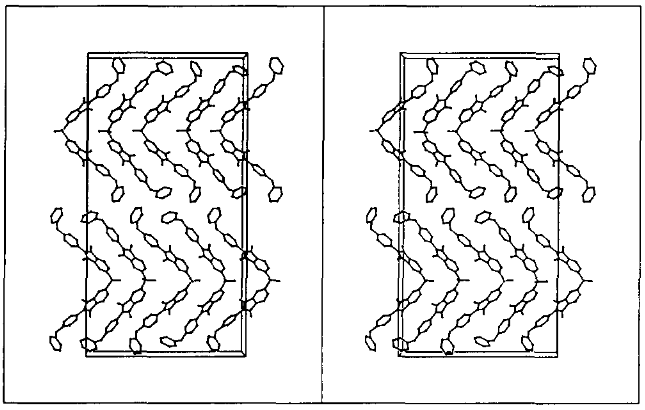

Figure 3 Stereoscopic view of the molecular packing in oligomer **4**

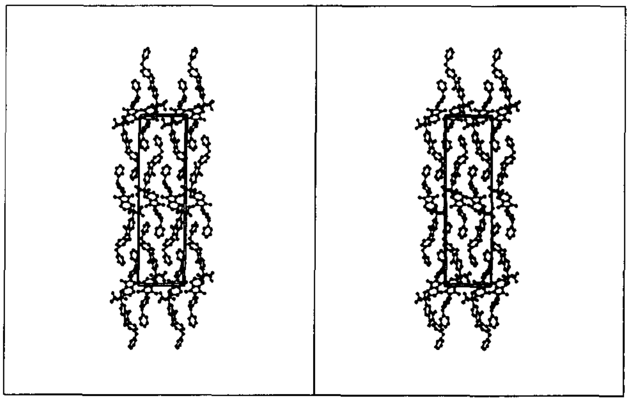

Figure 4 Stereoscopic view of the molecular packing in oligomer **5**

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

	x	*y*	*z*	*U*(eq)[a]
C(1)	−752(19)	660(4)	279(2)	81(4)
C(2)	−2481(21)	280(5)	225(5)	103(5)
C(3)	−2359(22)	−201(5)	362(2)	97(5)
C(4)	−580(22)	−303(4)	544(2)	88(5)
C(5)	1129(19)	82(4)	602(2)	80(4)
C(6)	974(16)	562(3)	463(2)	57(4)
O(6)	2702(11)	960(2)	509(1)	75(2)
C(7)	2505(17)	1272(3)	752(2)	56(3)
C(8)	4387(15)	1610(3)	807(2)	61(3)
C(9)	4303(15)	1951(3)	1036(2)	59(3)
C(10)	2358(16)	1943(3)	1213(2)	45(3)
C(11)	526(14)	1602(3)	1160(2)	53(3)
C(12)	555(15)	1259(3)	929(2)	57(3)
N(13)	2314(12)	2303(3)	1452(1)	49(3)
C(14)	3980(15)	2323(3)	1664(2)	47(3)
O(14)	5633(10)	2011(2)	1693(1)	69(2)
C(15)	3302(14)	2783(3)	1848(2)	43(3)
C(16)	4450(14)	2987(3)	2083(2)	53(3)
C(17)	3397(14)	3447(3)	2204(2)	48(3)
C(18)	1401(16)	3680(3)	2094(2)	58(3)
C(19)	286(14)	3462(3)	1857(2)	57(3)
C(20)	1344(14)	3007(3)	1740(2)	40(3)
C(21)	585(16)	2703(3)	1483(2)	50(3)
O(21)	−1108(10)	2771(2)	1331(1)	60(2)
S(22)	4742(7)	3755(2)	2500	70(1)
O(23)	7179(16)	3593(4)	2500	88(4)
O(24)	4025(19)	4323(3)	2500	102(4)
C(1′)	1265(16)	3431(3)	355(2)	65(3)
C(2′)	−287(19)	3383(4)	112(2)	77(4)
C(3′)	−2105(19)	3023(4)	125(2)	75(4)
C(4′)	−2401(20)	2717(4)	366(2)	96(5)
C(5′)	−837(17)	2775(4)	592(2)	76(4)
C(6′)	947(15)	3124(3)	573(2)	48(3)
O(6′)	2534(10)	3157(2)	798(1)	61(2)
C(7′)	2477(15)	3598(3)	981(2)	44(3)
C(8′)	617(14)	3958(3)	986(1)	47(3)
C(9′)	738(14)	4388(3)	1176(1)	44(3)
C(10′)	2652(15)	4446(3)	1348(2)	46(3)
C(11′)	4994(14)	4072(3)	1344(2)	50(3)
C(12′)	4403(14)	3649(3)	1158(2)	50(3)
N(13′)	2839(11)	4899(2)	1536(1)	44(2)
C(14′)	1256(14)	5029(3)	1752(2)	42(3)
O(14′)	−536(10)	4769(2)	1811(1)	57(2)
C(15′)	2173(13)	5513(3)	1894(1)	41(3)
C(16′)	1323(14)	5801(3)	2120(1)	47(3)
C(17′)	2684(15)	6240(3)	2208(1)	44(3)
C(18′)	4748(15)	6383(3)	2072(2)	47(3)
C(19′)	5597(14)	6092(3)	1842(2)	51(3)
C(20′)	4229(14)	5655(3)	1758(1)	42(3)
C(21′)	4701(15)	5273(3)	1523(2)	45(3)
O(21′)	6289(10)	5271(2)	1349(1)	55(2)
S(22′)	1693(6)	6627(1)	2500	55(1)
O(23′)	−856(13)	6623(3)	2500	69(3)
O(24′)	3024(15)	7127(3)	2500	70(3)
O(50)	7874(44)	185(9)	2500	147(8)

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

120° to 115.9(6)° and the adjacent angle O6–C7–C12 is correspondingly enlarged to 123.4(6)°. This type of structural distortion, which appears to be generic in aromatic ether oligomers[13,14], is discussed in more detail below.

The molecules of oligomer **4** pack in discrete, chevron-like lamellae (*Figure 3*), within which close, near-parallel ring-stacking (9° interplanar angle) occurs between the electronically complementary aminophenol (-NC_6H_4O-) and arene-imide [-Ar$(CO)_2$NAr′-] residues of adjacent molecules (*Figure 5*). The most significant contacts involve arene carbons C11′ and C12′, which lie 3.66 and 3.53 Å, respectively, above the imide plane. The opposite face of the imide is almost parallel to the imide group of a crystallographically independent molecule (3° interplanar angle), but here the geometric overlap is much less, involving only C17′ and a carbonyl oxygen O14, the latter lying some 3.60 Å below the imide plane. There are no significant intermolecular contacts involving the sulfone groups.

Perhaps the most striking conformational feature of oligomer **5** is its lack of symmetry (*Figure 2*). The terminal phenyl ether rings (C1–C6 and C42–C47) for example show torsion angles relative to their associated C–O–C planes of 30 and 16°, respectively, and the twist angles between the two chemically equivalent imide units

Table 2 Atomic coordinates ($\times 10^4$) and temperature factors (Å$^2 \times 10^3$) for oligomer **5**, with estimated standard deviations in parentheses

	x	*y*	*z*	*U*(eq)
C(1)	651(7)	1421(4)	3292(1)	86(2)
C(2)	426(8)	1783(4)	3591(1)	100(2)
C(3)	−1166(10)	1438(4)	3738(1)	112(3)
C(4)	−2494(10)	784(4)	3588(1)	119(3)
C(5)	−2296(7)	432(4)	3293(1)	95(2)
C(6)	−683(6)	746(3)	3149(1)	67(2)
O(7)	−500(5)	257(2)	2863(1)	101(1)
C(8)	490(7)	829(3)	2641(1)	67(2)
C(9)	−154(6)	1812(3)	2524(1)	76(2)
C(10)	742(6)	2308(3)	2281(1)	68(1)
C(11)	2265(5)	1774(3)	2165(1)	51(1)
C(12)	2899(6)	795(3)	2284(1)	83(2)
C(13)	2002(7)	301(4)	2525(1)	89(2)
N(14)	3243(4)	2265(2)	1915(1)	53(1)
C(15)	2559(5)	2225(3)	1602(1)	52(1)
O(15)	1052(4)	1843(2)	1501(1)	74(1)
C(16)	4127(5)	2737(3)	1429(1)	46(1)
C(17)	4199(5)	2932(3)	1114(1)	49(1)
C(18)	5864(5)	3439(3)	1014(1)	46(1)
C(19)	7366(5)	3730(3)	1231(1)	59(1)
C(20)	7254(5)	3534(3)	1547(1)	63(1)
C(21)	5625(5)	3034(3)	1639(1)	49(1)
C(22)	5085(5)	2746(3)	1955(1)	57(1)
O(22)	5966(4)	2899(2)	2202(1)	81(1)
C(23)	5924(5)	3752(3)	668(1)	48(1)
C(24)	5228(5)	4969(3)	637(1)	56(1)
F(24A)	6179(3)	5644(2)	840(1)	78(1)
F(24B)	3352(3)	5044(2)	691(1)	65(1)
F(24C)	5408(3)	5404(2)	357(1)	76(1)
C(25)	8002(6)	3685(4)	559(1)	69(2)
F(25A)	9153(3)	4503(2)	669(1)	82(1)
F(25B)	8870(3)	2729(2)	650(1)	87(1)
F(25C)	7978(3)	3725(2)	253(1)	96(1)
C(26)	4666(5)	2958(3)	453(1)	45(1)
C(27)	3265(5)	3325(3)	227(1)	46(1)
C(28)	2346(5)	2542(3)	37(1)	47(1)
C(29)	2755(5)	1419(3)	63(1)	48(1)
C(30)	4103(5)	1033(3)	286(1)	55(1)
C(31)	5040(5)	1814(3)	481(1)	52(1)
C(32)	793(5)	2700(3)	−216(1)	52(1)
O(32)	36(4)	3542(2)	−314(1)	67(1)
N(33)	365(4)	1615(2)	−333(1)	53(1)
C(34)	1536(5)	801(3)	−176(1)	56(1)
O(34)	1503(4)	−187(2)	−232(1)	70(1)
C(35)	−1212(5)	1369(3)	−556(1)	56(1)
C(36)	−2995(5)	1837(3)	−522(1)	63(1)
C(37)	−4548(6)	1576(3)	−728(1)	73(2)
C(38)	−4302(8)	824(4)	−959(1)	85(2)
C(39)	−2534(8)	364(4)	−997(1)	90(2)
C(40)	−954(6)	630(3)	−794(1)	76(2)
O(41)	−5938(5)	482(3)	−1144(1)	125(2)
C(42)	−6047(7)	674(4)	−1459(1)	81(2)
C(43)	−7452(7)	84(4)	−1622(1)	102(2)
C(44)	−7745(10)	305(7)	−1935(2)	142(4)
C(45)	−6667(11)	1061(7)	−2077(2)	139(4)
C(46)	−5249(9)	1614(5)	−1913(1)	115(3)
C(47)	−4927(8)	1428(4)	−1599(1)	99(2)

Table 3 Bond lengths (Å) for oligomer **4**, with estimated standard deviations in parentheses

C(1)–C(2)	1.381 (16)	C(1)–C(6)	1.326 (13)
C(2)–C(3)	1.363 (17)	C(3)–C(4)	1.341 (16)
C(4)–C(5)	1.385 (15)	C(5)–C(6)	1.365 (13)
C(6)–O(6)	1.407 (11)	O(6)–C(7)	1.386 (9)
C(7)–C(8)	1.376 (12)	C(7)–C(12)	1.380 (12)
C(8)–C(9)	1.377 (12)	C(9)–C(10)	1.378 (12)
C(10)–C(11)	1.359 (12)	C(10)–N(13)	1.438 (10)
C(11)–C(12)	1.385 (10)	N(13)–C(14)	1.372 (10)
N(13)–C(21)	1.401 (11)	C(14)–O(14)	1.219 (10)
C(14)–C(15)	1.489 (11)	C(15)–C(16)	1.377 (10)
C(15)–C(20)	1.338 (11)	C(16)–C(17)	1.411 (11)
C(17)–C(18)	1.366 (12)	C(17)–S(22)	1.763 (8)
C(18)–C(19)	1.394 (11)	C(19)–C(20)	1.393 (11)
C(20)–C(21)	1.489 (11)	C(21)–O(21)	1.205 (10)
S(22)–O(23)	1.430 (10)	S(22)–O(24)	1.472 (9)
S(22)–C(17A)	1.763 (8)	C(1′)–C(2′)	1.374 (13)
C(1′)–C(6′)	1.367 (11)	C(2′)–C(3′)	1.362 (14)
C(3′)–C(4′)	1.377 (14)	C(4′)–C(5′)	1.389 (14)
C(5′)–C(6′)	1.331 (12)	C(6′)–O(6′)	1.389 (10)
O(6′)–C(7′)	1.400 (9)	C(7′)–C(8′)	1.378 (11)
C(7′)–C(12′)	1.373 (11)	C(8′)–C(9′)	1.400 (10)
C(9′)–C(10′)	1.354 (11)	C(10′)–C(11′)	1.393 (11)
C(10′)–N(13′)	1.440 (9)	C(11′)–C(12′)	1.374 (10)
N(13′)–C(14′)	1.393 (10)	N(13′)–C(21′)	1.402 (10)
C(14′)–O(14′)	1.231 (9)	C(14′)–C(15′)	1.473 (10)
C(15′)–C(16′)	1.372 (10)	C(15′)–C(20′)	1.370 (10)
C(16′)–C(17′)	1.397 (11)	C(17′)–C(18′)	1.373 (11)
C(17′)–S(22′)	1.772 (7)	C(18′)–C(19′)	1.391 (10)
C(19′)–C(20′)	1.391 (11)	C(20′)–C(21′)	1.483 (10)
C(21′)–O(21′)	1.212 (10)	S(22′)–O(23′)	1.435 (8)
S(22′)–O(24′)	1.453 (8)	S(22′)–C(17B)	1.772 (7)

Table 4 Bond lengths (Å) for oligomer **5**, with estimated standard deviations in parentheses

C(1)–C(2)	1.383 (6)	C(1)–C(6)	1.344 (6)
C(2)–C(3)	1.375 (9)	C(3)–C(4)	1.339 (8)
C(4)–C(5)	1.359 (7)	C(5)–C(6)	1.371 (7)
C(6)–O(7)	1.380 (5)	O(7)–C(8)	1.398 (5)
C(8)–C(9)	1.344 (6)	C(8)–C(13)	1.350 (7)
C(9)–C(10)	1.393 (6)	C(10)–C(11)	1.359 (5)
C(11)–C(12)	1.340 (5)	C(11)–N(14)	1.444 (4)
C(12)–C(13)	1.384 (6)	N(14)–C(15)	1.400 (4)
N(14)–C(22)	1.398 (5)	C(15)–O(15)	1.191 (4)
C(15)–C(16)	1.493 (5)	C(16)–C(17)	1.383 (4)
C(16)–C(21)	1.374 (4)	C(17)–C(18)	1.399 (5)
C(18)–C(19)	1.391 (4)	C(18)–C(23)	1.543 (4)
C(19)–C(20)	1.391 (5)	C(20)–C(21)	1.363 (5)
C(21)–C(22)	1.481 (5)	C(22)–O(22)	1.203 (4)
C(23)–C(24)	1.538 (5)	C(23)–C(25)	1.549 (5)
C(23)–C(26)	1.552 (4)	C(24)–F(24A)	1.331 (4)
C(24)–F(24B)	1.339 (4)	C(24)–F(24C)	1.333 (4)
C(25)–F(25A)	1.329 (5)	C(25)–F(25B)	1.339 (5)
C(25)–F(25C)	1.322 (4)	C(26)–C(27)	1.394 (4)
C(26)–C(31)	1.398 (5)	C(27)–C(28)	1.372 (4)
C(28)–C(29)	1.377 (5)	C(28)–C(32)	1.489 (4)
C(29)–C(30)	1.373 (4)	C(29)–C(34)	1.482 (5)
C(30)–C(31)	1.388 (5)	C(32)–O(32)	1.198 (4)
C(32)–N(33)	1.417 (5)	N(33)–C(34)	1.409 (4)
N(33)–C(35)	1.431 (4)	C(34)–O(34)	1.207 (5)
C(35)–C(36)	1.373 (5)	C(35)–C(40)	1.378 (5)
C(36)–C(37)	1.379 (5)	C(37)–C(38)	1.364 (6)
C(38)–C(39)	1.363 (7)	C(38)–O(41)	1.399 (6)
C(39)–C(40)	1.389 (6)	O(41)–C(42)	1.376 (5)
C(42)–C(43)	1.356 (7)	C(42)–C(47)	1.361 (7)
C(43)–C(44)	1.378 (9)	C(44)–C(45)	1.350 (11)
C(45)–C(46)	1.343 (9)	C(46)–C(47)	1.378 (7)

and their adjacent aminophenol rings are 76° (about C11–N14) and 46° (about C35–N33). The central bridging unit is similarly unsymmetrical, with torsion angles between the aromatic rings and the bridging C–C–C plane of 27° (C16–C21) and 54° (C26–C31). However, the aminophenol (N–Ar–O) rings themselves are more or less symmetrically disposed with respect to the ether bridges, showing ring torsion angles of 60° (C8–C13) and 62° (C35–C40) relative to their associated C–O–C planes.

Bond angles in oligomer **5** are unexceptional for the most part; both nitrogen atoms are planar within experimental error, and the tetrahedral bridge-bond angle between the two imide residues (C18–C23–C26) is only slightly enlarged at 112°. Aromatic ether bridge-bond angles are normal at 119° (C6–O7–C8) and 120° (C38–O41–C42).

As in oligomer **4** however, there are very significant in-plane bending distortions at several of the arene carbons connected to bridging ether groups (e.g. C5–C6–O7 = 115°, C1–C6–O7 = 124°, and O41–C42–C43 = 114°; O41–C42–C47 = 124°). This type of distortion from ideal trigonal geometry was first recognized by Lindeman and co-workers[13], who pointed out a reciprocal relationship between the arene C–C–O bond-angle distortion and the corresponding torsion angle of the aromatic ring relative to the plane of its associated C–O–C bridging group.

This same relationship holds for both of the present

Table 5 Bond angles (°) for oligomer **4**, with estimated standard deviations in parentheses

C(2)–C(1)–C(6)	120.7(9)	C(1)–C(2)–C(3)	118.6(10)
C(2)–C(3)–C(4)	120.4(11)	C(3)–C(4)–C(5)	121.0(10)
C(4)–C(5)–C(6)	117.7(9)	C(1)–C(6)–C(5)	121.5(9)
C(1)–C(6)–O(6)	118.6(8)	C(5)–C(6)–O(6)	119.9(8)
C(6)–O(6)–C(7)	117.9(7)	O(6)–C(7)–C(8)	115.8(8)
O(6)–C(7)–C(12)	123.4(8)	C(8)–C(7)–C(12)	120.8(7)
C(7)–C(8)–C(9)	119.9(8)	C(8)–C(9)–C(10)	119.7(8)
C(9)–C(10)–C(11)	120.0(7)	C(9)–C(10)–N(13)	118.6(7)
C(11)–C(10)–N(13)	121.4(7)	C(10)–C(11)–C(12)	121.4(7)
C(7)–C(12)–C(11)	118.2(7)	C(10)–N(13)–C(14)	125.5(7)
C(10)–N(13)–C(21)	122.6(6)	C(14)–N(13)–C(21)	111.7(6)
N(13)–C(14)–O(14)	125.5(7)	N(13)–C(14)–C(15)	106.2(7)
O(14)–C(14)–C(15)	128.2(7)	C(14)–C(15)–C(16)	129.3(7)
C(14)–C(15)–C(20)	107.9(6)	C(16)–C(15)–C(20)	122.7(7)
C(15)–C(16)–C(17)	115.4(7)	C(16)–C(17)–C(18)	122.3(7)
C(16)–C(17)–S(22)	119.7(6)	C(18)–C(17)–S(22)	118.0(6)
C(17)–C(18)–C(19)	120.7(7)	C(18)–C(19)–C(20)	116.3(7)
C(15)–C(20)–C(19)	122.6(7)	C(15)–C(20)–C(21)	109.6(7)
C(19)–C(20)–C(21)	127.8(7)	N(13)–C(21)–C(20)	104.5(7)
N(13)–C(21)–O(21)	125.8(7)	C(20)–C(21)–O(21)	129.7(7)
C(17)–S(22)–O(23)	106.8(4)	C(17)–S(22)–O(24)	107.5(4)
O(23)–S(22)–O(24)	122.3(6)	C(17)–S(22)–C(17A)	104.6(5)
O(23)–S(22)–C(17A)	106.8(4)	O(24)–S(22)–C(17A)	107.5(4)
C(2′)–C(1′)–C(6′)	119.8(8)	C(1′)–C(2′)–C(3′)	119.9(8)
C(2′)–C(3′)–C(4′)	119.5(9)	C(3′)–C(4′)–C(5′)	119.9(10)
C(4′)–C(5′)–C(6′)	119.6(8)	C(1′)–C(6′)–C(5′)	121.3(8)
C(1′)–C(6′)–O(6′)	120.6(7)	C(5′)–C(6′)–O(6′)	118.1(7)
C(6′)–O(6′)–C(7′)	120.2(6)	O(6′)–C(7′)–C(8′)	122.6(7)
O(6′)–C(7′)–C(12′)	115.4(7)	C(8′)–C(7′)–C(12′)	122.0(7)
C(7′)–C(8′)–C(9′)	118.1(7)	C(8′)–C(9′)–C(10′)	120.2(7)
C(9′)–C(10′)–C(11′)	121.0(7)	C(9′)–C(10′)–N(13′)	120.6(7)
C(11′)–C(10′)–N(13′)	118.4(7)	C(10′)–C(11′)–C(12′)	119.5(7)
C(7′)–C(12′)–C(11′)	119.2(7)	C(10′)–N(13′)–C(14′)	125.9(6)
C(10′)–N(13′)–C(21′)	123.3(6)	C(14′)–N(13′)–C(21′)	110.8(6)
N(13′)–C(14′)–O(14′)	124.7(7)	N(13′)–C(14′)–C(15′)	107.4(6)
O(14′)–C(14′)–C(15′)	127.9(7)	C(14′)–C(15′)–C(16′)	131.3(7)
C(14′)–C(15′)–C(20′)	107.1(6)	C(16′)–C(15′)–C(20′)	121.6(7)
C(15′)–C(16′)–C(17′)	116.6(7)	C(16′)–C(17′)–C(18′)	122.0(7)
C(16′)–C(17′)–S(22′)	118.9(6)	C(18′)–C(17′)–S(22′)	119.1(6)
C(17′)–C(18′)–C(19′)	121.2(7)	C(18′)–C(19′)–C(20′)	116.2(7)
C(15′)–C(20′)–C(19′)	122.3(7)	C(15′)–C(20′)–C(21′)	109.6(7)
C(19′)–C(20′)–C(21′)	128.1(7)	N(13′)–C(21′)–C(20′)	105.1(6)
N(13′)–C(21′)–O(21′)	125.2(7)	C(20′)–C(21′)–O(21′)	129.7(7)
C(17′)–S(22′)–O(23′)	108.1(3)	C(17′)–S(22′)–O(24′)	107.7(3)
O(23′)–S(22′)–O(24′)	121.4(5)	C(17′)–S(22′)–C(17B)	102.2(5)
O(23′)–S(22′)–C(17B)	108.1(3)	O(24′)–S(22′)–C(17B)	107.7(3)

structures. The plane of ring C42–C47 in oligomer **5** lies close to the plane of the ether bridge C38–O41–C42 (the average torsion is only 16°). There is thus a substantial steric interaction between the *ortho*-hydrogen atom at C47 and the adjacent aromatic ring C35–C40. This in turn leads, as shown in *Figure 6*, to an in-plane distortion at C42 of some 5° (an enlargement of the angle O41–C42–C47). On the other hand, the ring C35–C40 adopts a very much higher torsion angle (60°) relative to the bridging C–O–C plane, so that its *ortho*-hydrogens lie almost clear of the adjacent ring and there is thus only minimal distortion (1–2°) from ideal geometry at

Table 6 Bond angles (°) for oligomer **5**, with estimated standard deviations in parentheses

C(2)–C(1)–C(6)	120.0(4)	C(1)–C(2)–C(3)	119.1(5)
C(2)–C(3)–C(4)	119.8(5)	C(3)–C(4)–C(5)	121.6(6)
C(4)–C(5)–C(6)	118.9(5)	C(1)–C(6)–C(5)	120.6(4)
C(1)–C(6)–O(7)	124.3(4)	C(5)–C(6)–O(7)	115.0(4)
C(6)–O(7)–C(8)	119.1(3)	O(7)–C(8)–C(9)	121.4(4)
O(7)–C(8)–C(13)	117.2(4)	C(9)–C(8)–C(13)	121.0(4)
C(8)–C(9)–C(10)	120.3(4)	C(9)–C(10)–C(11)	118.4(4)
C(10)–C(11)–C(12)	120.9(3)	C(10)–C(11)–N(14)	120.1(3)
C(12)–C(11)–N(14)	119.0(3)	C(11)–C(12)–C(13)	120.6(4)
C(8)–C(13)–C(12)	118.8(4)	C(11)–N(14)–C(15)	124.5(3)
C(11)–N(14)–C(22)	123.3(2)	C(15)–N(14)–C(22)	111.9(3)
N(14)–C(15)–O(15)	126.1(3)	N(14)–C(15)–C(16)	105.2(3)
O(15)–C(15)–C(16)	128.7(3)	C(15)–C(16)–C(17)	129.8(3)
C(15)–C(16)–C(21)	108.5(3)	C(17)–C(16)–C(21)	121.7(3)
C(16)–C(17)–C(18)	117.9(3)	C(17)–C(18)–C(19)	119.4(3)
C(17)–C(18)–C(23)	119.2(3)	C(19)–C(18)–C(23)	121.2(3)
C(18)–C(19)–C(20)	121.7(3)	C(19)–C(20)–C(21)	117.9(3)
C(16)–C(21)–C(20)	121.4(3)	C(16)–C(21)–C(22)	108.6(3)
C(20)–C(21)–C(22)	130.0(3)	N(14)–C(22)–C(21)	105.8(3)
N(14)–C(22)–O(22)	124.8(3)	C(21)–C(22)–O(22)	129.4(3)
C(18)–C(23)–C(24)	106.5(3)	C(18)–C(23)–C(25)	112.0(3)
C(24)–C(23)–C(25)	108.3(3)	C(18)–C(23)–C(26)	112.2(3)
C(24)–C(23)–C(26)	111.7(3)	C(25)–C(23)–C(26)	106.1(3)
C(23)–C(24)–F(24A)	112.4(3)	C(23)–C(24)–F(24B)	110.5(3)
F(24A)–C(24)–F(24B)	106.4(3)	C(23)–C(24)–F(24C)	113.6(3)
F(24A)–C(24)–F(24C)	106.7(3)	F(24B)–C(24)–F(24C)	106.8(3)
C(23)–C(25)–F(25A)	113.4(3)	C(23)–C(25)–F(25B)	111.1(3)
F(25A)–C(25)–F(25B)	106.3(3)	C(23)–C(25)–F(25C)	111.1(3)
F(25A)–C(25)–F(25C)	107.2(3)	F(25B)–C(25)–F(25C)	107.4(3)
C(23)–C(26)–C(27)	123.9(3)	C(23)–C(26)–C(31)	117.1(3)
C(27)–C(26)–C(31)	119.0(3)	C(26)–C(27)–C(28)	118.1(3)
C(27)–C(28)–C(29)	122.4(3)	C(27)–C(28)–C(32)	129.1(3)
C(29)–C(28)–C(32)	108.4(3)	C(28)–C(29)–C(30)	120.7(3)
C(28)–C(29)–C(34)	109.2(3)	C(30)–C(29)–C(34)	130.1(3)
C(29)–C(30)–C(31)	117.6(3)	C(26)–C(31)–C(30)	122.2(3)
C(28)–C(32)–O(32)	129.7(3)	C(28)–C(32)–N(33)	105.4(3)
O(32)–C(32)–N(33)	125.0(3)	C(32)–N(33)–C(34)	111.5(3)
C(32)–N(33)–C(35)	123.8(3)	C(34)–N(33)–C(35)	124.3(3)
C(29)–C(34)–N(33)	105.4(3)	C(29)–C(34)–O(34)	129.0(3)
N(33)–C(34)–O(34)	125.5(3)	N(33)–C(35)–C(36)	119.4(3)
N(33)–C(35)–C(40)	120.0(3)	C(36)–C(35)–C(40)	120.5(3)
C(35)–C(36)–C(37)	120.2(3)	C(36)–C(37)–C(38)	119.2(4)
C(37)–C(38)–C(39)	121.2(4)	C(37)–C(38)–O(41)	118.2(4)
C(39)–C(38)–O(41)	120.5(4)	C(38)–C(39)–C(40)	120.0(4)
C(35)–C(40)–C(39)	118.8(4)	C(38)–O(41)–C(42)	120.0(4)
O(41)–C(42)–C(43)	114.3(4)	O(41)–C(42)–C(47)	124.0(4)
C(43)–C(42)–C(47)	121.7(4)	C(42)–C(43)–C(44)	117.2(5)
C(43)–C(44)–C(45)	122.0(6)	C(44)–C(45)–C(46)	119.8(6)
C(45)–C(46)–C(47)	120.0(6)	C(42)–C(47)–C(46)	119.3(5)

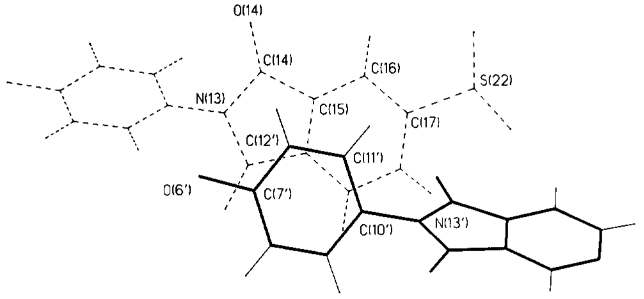

Figure 5 Molecular stacking in the crystal structure of oligomer **4**, projected perpendicular to the plane of the ring C7′–C12′

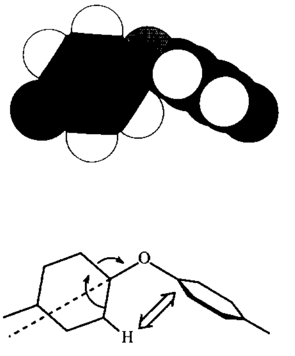

Figure 6 Steric effects in a diarylene ether residue showing how C–C–O bond-angle distortions can be generated by an *ortho*-hydrogen interacting with the adjacent aromatic ring

Table 7 Selected torsional angles (°) for oligomer **4** (two independent half-molecules), with estimated standard deviations in parentheses

C(1)–C(6)–O(6)–C(7)	101.5(7)	C(1′)–C(6′)–O(6′)–C(7′)	75.6(7)
C(5)–C(6)–O(6)–C(7)	−80.0(8)	C(5′)–C(6′)–O(6′)–C(7′)	−106.6(7)
C(6)–O(6)–C(7)–C(8)	172.2(6)	C(6′)–O(6′)–C(7′)–C(8′)	13.3(8)
C(6)–O(6)–C(7)–C(12)	−8.6(9)	C(6′)–O(6′)–C(7′)–C(12′)	−167.0(9)
C(9)–C(10)–N(13)–C(14)	−58.0(8)	C(9′)–C(10′)–N(13′)–C(14′)	60.4(8)
C(9)–C(10)–N(13)–C(21)	118.1(7)	C(9′)–C(10′)–N(13′)–C(21′)	−119.9(6)
C(11)–C(10)–N(13)–C(14)	122.4(7)	C(11′)–C(10′)–N(13′)–C(14′)	−120.5(6)
C(11)–C(10)–N(13)–C(21)	−61.6(8)	C(11′)–C(10′)–N(13′)–C(21′)	59.1(7)
C(16)–C(17)–S(22)–O(23)	21.3(6)	C(16′)–C(17′)–S(22′)–O(23′)	−32.3(6)
C(16)–C(17)–S(22)–O(24)	154.2(5)	C(16′)–C(17′)–S(22′)–O(24′)	−161.5(5)
C(16)–C(17)–S(22)–C(17a)	−91.7(5)	C(16′)–C(17′)–S(22′)–C(17b)	81.6(6)
C(18)–C(17)–S(22)–O(23)	−156.0(5)	C(18′)–C(17′)–S(22′)–O(23′)	147.0(5)
C(18)–C(17)–S(22)–O(24)	−23.1(6)	C(18′)–C(17′)–S(22′)–O(24′)	14.2(6)
C(18)–C(17)–S(22)–O(17a)	90.9(5)	C(18′)–C(17′)–S(22′)–O(17b)	−99.1(5)

Table 8 Selected torsional angles (°) for oligomer **5**, with estimated standard deviations in parentheses

C(1)–C(6)–O(7)–C(8)	−32.9(5)	C(19)–C(18)–C(23)–C(26)	155.4(3)
C(5)–C(6)–O(7)–C(8)	151.8(3)	C(18)–C(23)–C(26)–C(27)	128.2(3)
C(6)–O(7)–C(8)–C(9)	−62.9(4)	C(18)–C(23)–C(26)–C(31)	−54.7(3)
C(6)–O(7)–C(8)–C(13)	123.9(4)	C(24)–C(23)–C(26)–C(27)	8.7(4)
C(10)–C(11)–N(14)–C(15)	−79.5(4)	C(24)–C(23)–C(26)–C(31)	−174.2(3)
C(10)–C(11)–N(14)–C(22)	106.9(3)	C(25)–C(23)–C(26)–C(27)	−109.1(3)
C(12)–C(11)–N(14)–C(15)	101.4(4)	C(25)–C(23)–C(26)–C(31)	68.0(3)
C(12)–C(11)–N(14)–C(22)	−72.2(4)	C(32)–N(33)–C(35)–C(36)	44.1(4)
C(17)–C(18)–C(23)–C(24)	92.7(3)	C(34)–N(33)–C(35)–C(36)	128.1(3)
C(17)–C(18)–C(23)–C(25)	−149.0(3)	C(39)–C(38)–O(41)–C(42)	−64.4(5)
C(17)–C(18)–C(23)–C(26)	−29.7(4)	C(38)–O(41)–C(42)–C(43)	165.2(4)
C(19)–C(18)–C(23)–C(24)	−82.1(3)	C(32)–N(33)–C(35)–C(40)	138.8(3)
C(19)–C(18)–C(23)–C(25)	36.2(4)	C(34)–N(33)–C(35)–C(40)	−49.0(4)
C(19)–C(18)–C(23)–C(26)	155.4(3)	C(37)–C(38)–O(41)–C(42)	119.5(4)
		C(38)–O(41)–C(42)–C(47)	−18.0(6)

C38 (cf. *Figure 6*). Perhaps the most extreme example of this effect so far discovered is in the (centrosymmetric) structure of oligoimide **1**[4], where both aromatic rings adjacent to the ether bridge lie close to the C–O–C plane (average torsion angle 24°) and the associated C–C–O bond angles (internal and external) average 126 and 112°, respectively. Although very large torsion-related bond angle distortions (up to 8°) are clearly possible at arene carbon atoms in poly(aryl ether)s, it seems remarkable that, contradicting molecular mechanics predictions for such systems[15], the bridge-bond (C–O–C) angle remains essentially constant at $120 \pm 2°$.

Molecules of oligomer **5** pack in a linearly displaced, non-lamellar fashion in the crystal, the structure showing no evidence for parallel stacking of electronically complementary sub-units (*Figure 4*). This absence of close-stacking clearly demonstrates the effectiveness of the $-C(CF_3)_2-$ linkage at disrupting extended intermolecular associations. There are indeed few exceptionally close intermolecular contacts of any sort, the only interaction of note being a pairwise carbonyl–carbonyl contact (C....O = 2.94 Å) involving the orthogonal approach of O34 to C34′ (and O34′ to C34). The fluorine atoms of neighbouring chains lie somewhat adjacent in the crystal, but make no significant intermolecular contacts. Even the shortest contact involving fluorine (C=O....F = 2.88 Å) is substantially greater than the sum of the corresponding van der Waals radii (2.75 Å).

Overall, the distinctly irregular conformation and non-stacked crystal structure of oligomer **5** provide good experimental support for the proposed role of 6FDA (see Introduction) in achieving desirable materials properties such as processability, solubility, absence of colour, and high permeability in aromatic polyimides.

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