Single-Crystal X-ray Studies of Aromatic Oligomers: Conformation and Packing in Isomeric Pyromellitimide–Ether–Sulfones

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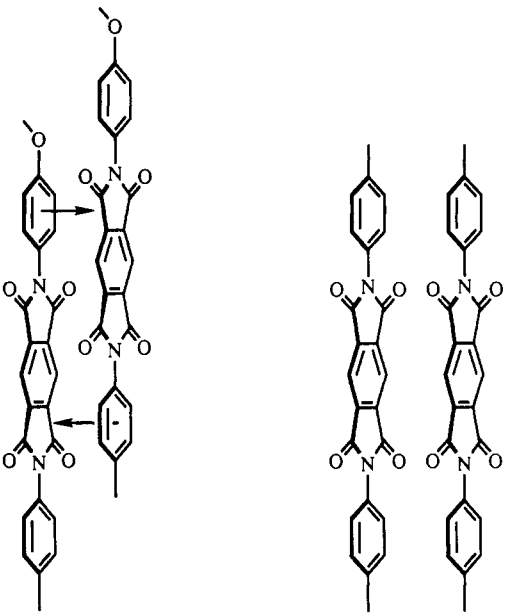
ABSTRACT: The crystal and molecular structures of two isomeric, aromatic, pyromellitimide oligomers **1** and **2** have been determined by single-crystal X-ray diffraction. Crystal data for **1** ($C_{46}H_{28}N_2O_{10}S_2$): triclinic, $P\bar{1}$; a = 8.038 (3), b = 10.947 (3), c = 11.308 (4) Å; α = 95.75 (3), β = 105.79 (2), γ = 92.89 (3)°. Crystal data for **2** ($C_{46}H_{28}N_2O_{10}S_2$): monoclinic, $P2_1/a$; a = 11.844 (5), b = 6.977 (2), c = 22.694 (6) Å; β = 101.96 (3)°. The structure of the yellow isomer (**2**) provides the first direct evidence of complementary, face-to-face stacking between electron-rich imidophenoxy (N–Ar–O) and electron-poor pyromellitimide units in adjacent chains, an association long suspected but not yet conclusively demonstrated in aromatic polyimides. In contrast, the colorless oligomer (**1**) adopts a packing mode in which all the parallel ring–ring contacts occur between aromatic systems of like, rather than complementary, electronic character.

Introduction

High-performance aromatic polyimides have been subjected to intensive study since their commercial introduction some 30 years ago.[1] Many investigations have been directed toward achieving an understanding, at the molecular level, of characteristic polyimide properties such as color, fluorescence, photoconductivity, unusual resistance to solvent attack, and high glass transition temperatures. Since aromatic polyimide molecules generally contain an alternating sequence of electron-rich and electron-poor subunits, it has often been suggested that some or all of these properties may depend on the existence of intermolecular charge-transfer interactions between electronically complementary regions of the polyimide chains.[2]

The importance of charge-transfer in polyimides may, however, have been overemphasized in the past, since known T_g–structure relationships have recently been accounted for quite satisfactorily in steric terms,[3] without recourse to a charge-transfer model. Moreover, it has long been known that, even in classical "charge-transfer complexes", intermolecular interactions are actually dominated by dipolar and dispersive forces.[4] There has even been doubt as to whether the characteristic "charge-transfer" absorption of polyimides in the visible region should be assigned to an *inter*molecular or *intra*molecular process.[5] Nevertheless, a recent high-pressure spectroscopic investigation provides very strong support for the existence of intermolecular charge-transfer absorptions in the visible spectrum of poly[bis(4-phenoxyphenyl)pyromellitimide] film[6] and thus suggests that adjacent stacking of (electron-rich) imidophenoxy and (electron-poor) pyromellitimide units must indeed occur in the solid state (Figure 1a).

So far as we are aware, however, there is no clear-cut *structural* evidence for this type of association between polyimide chains. X-ray diffraction studies of a series of aromatic polyimides[7] suggest that the chains pack "in register" so that adjacent stacking of electronically complementary subunits in the crystalline state is not observed (Figure 1b). Charge-transfer transitions could, however, be equally well attributed to *non*crystalline regions of the polymer, and indeed the most intensively studied polyimide, poly[bis(4-phenoxyphenyl)pyromellitimide] (Du Pont's Kapton), is normally characterized by a very low level of crystalline order.[8]



(a) (b)

Figure 1. (a) Potential charge-transfer interactions in poly[bis(4-phenoxyphenyl)pyromellitimide]; (b) "in-register" chains in crystalline poly(pyromellitimides).

The crystal structure of poly[bis(4-phenoxyphenyl)pyromellitimide] has not in fact been fully established; the

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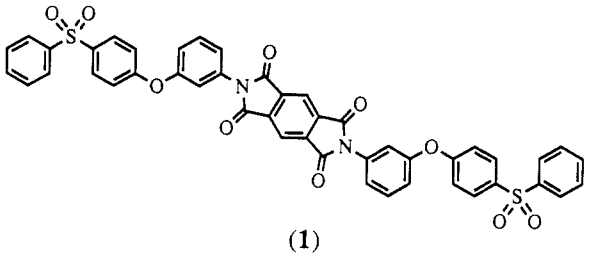
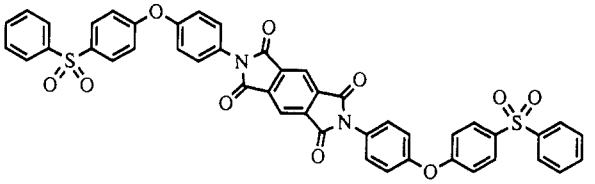


(1)



(2)

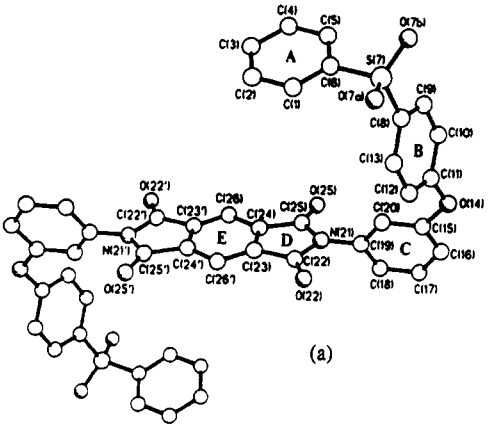
two reported X-ray fiber diffraction studies give conflicting results even for the crystal system and unit cell.[9] The value of *single-crystal oligomer X-ray data* in providing structural information for the determination of polymer structure and for the modeling of polymer behavior is, however, becoming steadily more apparent.[10] In an attempt to resolve some of the structural uncertainties surrounding polyimides, we have synthesized and determined the crystal structures of the isomeric oligoimides **1** and **2**. We now report conformational and crystal packing data which provide, for the first time, unambiguous evidence of electronically complementary stacking between aromatic pyromellitimide chains.

Results

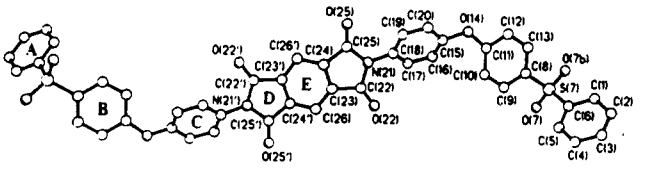
The isomeric diamines **3** and **4** were prepared (Scheme I) by reaction of 3- or 4-aminophenol, respectively, with 4-chlorophenyl phenyl sulfone in the presence of potassium carbonate. Condensation of **3** and **4** with pyromellitic dianhydride yielded the oligomeric imides **1** and **2** in ca. 40% yield after crystallization.[11] Single crystals of **1** and **2**, suitable for X-ray analysis, were grown by slow evaporation of solutions in *N*-methylpyrrolidone (**1**) or in dichloromethane/chlorobenzene (**2**).[12]

X-ray analysis revealed that the oligomer molecules (Figure 2) adopt strikingly different conformations in the solid state.[13] The oligomer **1**, derived from 3-aminophenol, takes up a centrosymmetric S-shaped conformation in which the terminal phenylsulfonyl groups A are folded back toward the center of the molecule and are positioned approximately parallel to and overlying their associated imide functions D (centroid–centroid distance, A–D = 7.48 Å). This geometry is achieved by a combination of (i) a relationship between the imide unit D and the 3-imidophenoxy residue C which is nearer orthogonal than planar (average inter-ring torsion angle 73°), (ii) a similar relationship between rings C and B (118° bond angle at oxygen, 70° between mean planes), and (iii) a conventional "open-book" conformation (104° bond angle at sulfur) for the terminal diphenyl sulfone unit (torsion angles, C(1)C(6)S(7)C(8) = 96° and C(6)S(7)C(8)C(9) = 91°).

In contrast, the all-para oligomer **2**, which is also centrosymmetric, adopts a much more generally flattened and extended conformation, with an average inter-ring torsion angle between the imide unit D and the 4-aminophenol residue C of only 38°. The ether bond angle between rings C and B is 121°, and the angle between their mean planes is 39°. This latter rotation is such as to bring ring B almost into coplanarity with the central



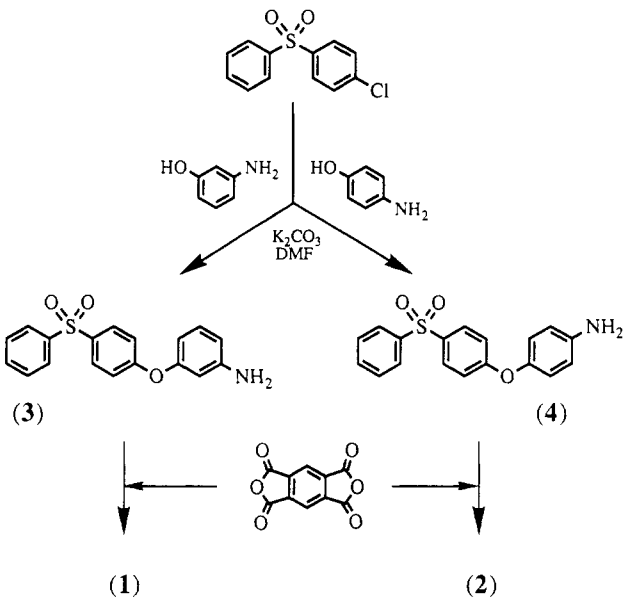
(a)



(b)

Figure 2. Molecular structures of (a) oligomer **1** and (b) oligomer **2**, with atom numbering and ring identifiers.

Scheme I
Synthesis of Oligomers 1 and 2



pyromellitimide fragment (14° between the mean planes). The geometry of the diphenyl sulfone residue (bond angle at sulfur of 106°) is similar to that observed in oligomer **1**, though with slightly greater deviations from ideal geometry (torsion angles C(1)C(6)S(7)C(8) = 113° and C(6)S(7)C(8)C(9) = 80°).

Associated with these contrasting conformations are very significant differences in molecular packing. In **1**, the near-parallel alignment of rings A and D, coupled with the ca. 7.5-Å (A–D) ring–ring separation, allows insertion of the terminal sulfone-bearing ring A of a symmetry-related molecule (Figure 3), so creating an infinite face-to-face stacking arrangement between the arene-sulfone and pyromellitimide rings (interplanar separations: A–A′ = 3.55 Å, A–D′ = 3.73 Å). Furthermore, within this arrangement there are aromatic edge-to-face interactions (centroid–

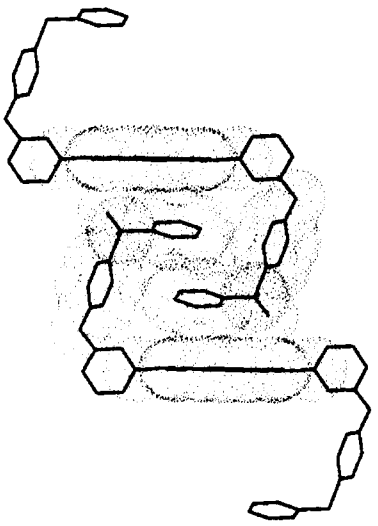


Figure 3. Intermolecular contacts in the crystal structure of oligomer 1. Dotted areas indicate van der Waals surfaces.

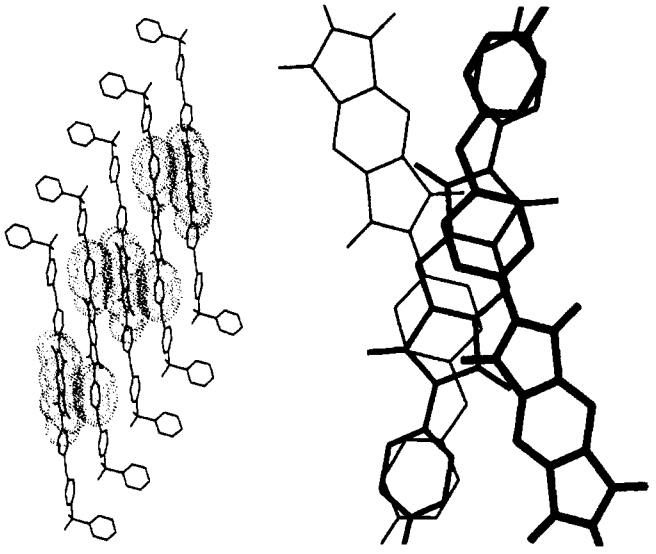


Figure 4. (a) Intermolecular contacts in the crystal structure of oligomer 2, highlighting the electronically complementary stacking of imidophenoxy and pyromellitimide groups. (b) The same interaction for three adjacent chains, projected perpendicular to the central pyromellitimide unit.

centroid distance 5.4 Å) between the terminal arene group (ring A) of one molecule and the ether-sulfone ring (B) of its interlocking neighbor (Figure 3). The pyromellitimide unit also interacts particularly strongly with a sulfone oxygen of an adjacent molecule [O(7b)...C(25), 3.07 Å; O(7b)...N(21), 3.08 Å; O(7b)...C(22), 3.12 Å]. These close interatomic contacts are consistent with a strong electrostatic interaction between the negatively polarized sulfone oxygen and a positively polarized region associated with the C–N–C unit of the imide ring.

The more extended molecules of oligomer 2 pack in lamella-like fashion, with the lamella plane inclined at some 36° to the long axis of the molecule (Figure 4). The terminal arene-sulfone rings again interlock but now in an edge-to-face rather than face-to-face orientation. There are a number of close, intermolecular, carbonyl–carbonyl contacts, but perhaps more significantly *there is an approximately parallel overlap of the pyromellitimide unit of one molecule with the 4-imidophenoxy residue of its closest neighbor* (mean interplanar separation C–D′ = 3.39 Å).

Discussion

The close and parallel overlap in oligomer 2 between an electron-rich 4-imidophenoxy ring of one chain and an electron-deficient pyromellitimide unit of an adjacent chain is certainly consistent with the proposed existence of intermolecular charge-transfer interactions in aromatic polyimides.[2,6] In the present oligomer structure, complementary interactions extend in stepwise fashion throughout the crystal (Figure 4). The geometry of this particular contact places the HOMO (associated principally with an imidophenoxy unit) of one oligomer directly adjacent to the LUMO (localized essentially on the pyromellitimide residue) of its closest neighbor.[14] An interchain charge-transfer transition (HOMO → LUMO) may well therefore be responsible for the intense yellow color of compound 2 in the solid state. However, the relatively planar conformation of this oligomer will also favor electron delocalization via *intra*chain charge transfer,[5] and indeed a dilute (1% w/v) solution of oligomer 2 in NMP does retain a faint but perceptible color. A quantitative study of absorbance as a function of concentration is clearly needed to resolve the relative contributions of inter- and intramolecular transitions to the visible spectrum of this compound.

Oligomer 1 is essentially colorless, both in the solid state and in solution. This suggests an absence of charge-transfer interactions, and indeed in the crystal structure of 1 (Figure 3) all the parallel ring–ring contacts occur between aromatic systems of like, rather than opposite, electronic character. Moreover, assuming the crystal structures to represent conformational ground states, the much greater deviations from ring–ring coplanarity in oligomer 1, when compared with oligomer 2, would also tend to restrict *intra*molecular charge transfer.

Conclusions

Even though this work provides firm evidence for electronically complementary self-stacking of pyromellitimide chains, it is clear that further work is needed to correlate this type of interaction with optical properties and to disentangle contributions from intermolecular (packing) and intramolecular (conformational) effects. It must also be borne in mind that charge transfer per se makes only a very small contribution to ground-state intermolecular binding energies. It has recently been pointed out that intermolecular charge transfer in many systems is in fact mainly a consequence of, rather than a driving force for, complementary π–π stacking,[15] and our own theoretical studies indicate that this conclusion is also valid for the oligomer structures reported here.[16]

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Supplementary Material Available: Listings of crystal data, positional and thermal parameters, bond lengths and angles, and torsion angles for 1 and 2 (14 pages). Ordering information is given on any current masthead page.

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(11) Oligomer **1** had mp 380–384 °C. Elem. anal. Calcd for $C_{46}H_{28}N_2O_{10}S_2$: C, 66.3; H, 3.3; N, 3.3. Found: C, 65.6; H, 3.3; N, 3.1. Oligomer **2**, isomeric with **1**, had mp 378–380 °C. Elem. anal. Found: C, 65.9; H, 3.3; N, 3.1. Both compounds gave satisfactory infrared, ^{1}H NMR, and mass spectra.
(12) Crystal data for **1** ($C_{46}H_{28}N_2O_{10}S_2$): triclinic, $P\bar{1}$,; a = 8.038 (3), b = 10.947 (3), c = 11.308 (4) Å; α = 95.75 (3), β = 105.79 (2), γ = 92.89 (3)°; V = 950 Å^3; Z = 1 (the molecule has a crystallographic center of symmetry); D(calcd) = 1.46 g cm^{-3}. Crystal data for **2** ($C_{46}H_{28}N_2O_{10}S_2$): monoclinic, $P2_1/a$; a = 11.844 (5), b = 6.977 (2), c = 22.694 (6) Å; β = 101.96 (3)°; V = 1835 Å^3; Z = 2 (the molecule has a crystallographic center of symmetry); D(calcd) = 1.51 g cm^{-3}.
(13) All X-ray data were collected with a Nicolet R3m diffractometer (Cu Kα radiation) using ω scans. The 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. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. For **1**, 2559 independent reflections ($2\theta \leq 116°$) were measured, of which 1245 were considered observed ($|F_o| > 3\sigma|F_o|$). Refinement by block-cascade, full-matrix least squares gave an R factor of 0.084, R_w = 0.077. The final R factor for this structure probably reflects rather poor crystal quality, as a result of a tendency to twinning. For **2**, 2472 independent reflections ($2\theta \leq 116°$) were measured, of which 1610 were considered observed ($|F_o| > 3\sigma|F_o|$). Refinement by block-cascade, full-matrix least squares gave an R factor of 0.074, R_w = 0.065. All computations were carried out using the SHELXTL program system.[17]
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Registry No. **1**, 136862-84-5; **2**, 136862-85-6; **3**, 136862-86-7; **4**, 94905-61-0; PMDA, 89-32-7.