A synchrotron diffraction study of two polymorphic forms of 2,5-bis-[2-(4-methoxyphenyl)ethenyl]pyrazine

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Two polymorphs, α and γ, of the title compound, $C_{22}H_{20}N_2O_2$, have been characterized by means of single-crystal synchrotron X-ray diffraction. In the α form, the molecules pack in a herring-bone fashion, linked *via* weak $C-H\cdots N$ intermole-

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cular interactions ($H\cdots N$ 2.58 Å). In the γ form, the molecules are arranged in nearly planar sheets, which form a network held together by intermolecular hydrogen bonds of the type $C-H\cdots O$ ($H\cdots O$ 2.49 Å) and $C-H\cdots N$ ($H\cdots N$ 2.50 Å). The stacking distance between the sheets is 3.40 Å.

Comment

The discovery that semiconducting polymers based on poly-phenylenevinylene (PPV) have interesting and useful elec-troluminescent properties has led to their successful development as components in light-emitting diodes (LEDs) and other semiconducting devices (Burroughes *et al.*, 1990; Braun & Heeger, 1991). The characteristics and efficiencies of these devices have been improved by the introduction of electron-withdrawing substituents on the PPV backbone which lower the barrier to electron injection (Bredas & Heeger, 1994). Another way to achieve high electron affinity is to incorporate electronegative hetero atoms into the polymer backbone. Evidence for this has been found in work on

(I)
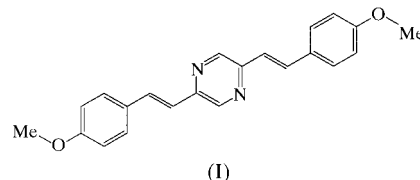
oligomers based on distyrylpyrazine which show promise as emissive and/or charge-transport agents for LED devices. In particular, devices made with the dimethoxy derivative 2,5-bis[2-(4-methoxyphenyl)ethenyl]pyrazine, (I), have been
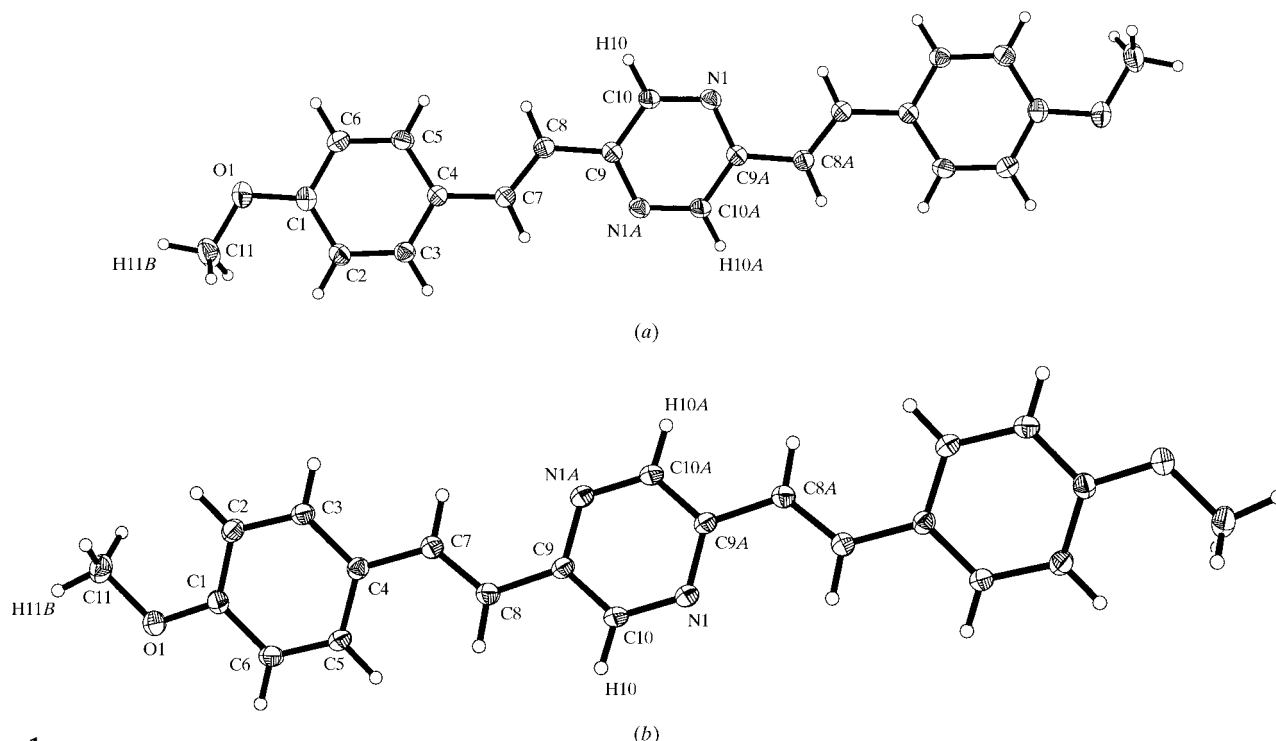

Figure 1
The molecular structures of (*a*) the α form and (*b*) the γ form of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

shown to have a higher electron affinity than PPV itself (Nohara *et al.*, 1990; Grimsdale *et al.*, 1997). To understand this effect properly, it is necessary first to obtain a detailed knowledge of the structure of the oligomer in the solid state. The parent compound, 2,5-distyrylpyrazine, has two known polymorphic forms, an orthorhombic α-form (Sasada *et al.*, 1971) and a monoclinic γ-form (Nakanishi *et al.*, 1976); the very similar polymorphic forms found for the title dimethoxy derivative, (I), have accordingly been denoted α and γ.

Preliminary measurements were made on laboratory X-ray diffractometers, but due to the weak diffraction of both forms it was necessary to exploit the high intensity of a synchrotron radiation source to determine the crystal structures accurately. These determinations represent the first reported crystal structures of a substituted 2,5-distyrylpyrazine.
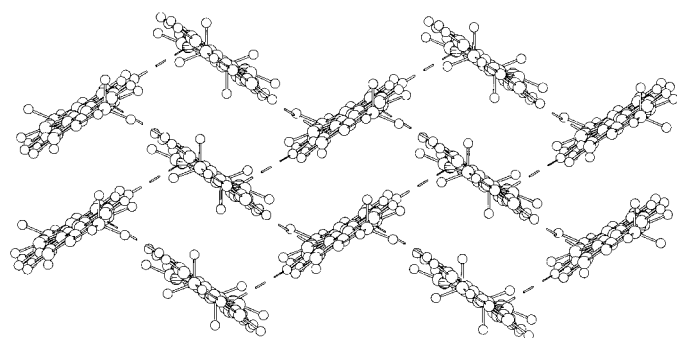

Figure 2
The herring-bone type of packing in the α-form of (I), showing the C—H···N intermolecular interactions (H···N 2.58 Å).

Both forms of (I) have one half molecule in the asymmetric unit and the two rings attached to each double bond are mutually *trans*. The bond lengths and angles are comparable, but there is a difference in the molecular planarity of the two forms caused by differences in the reciprocal orientation of the aromatic rings. Molecules in the γ-form are slightly more planar, with r.m.s. torsional deviations from planarity of 3.5 (2) and 3.3 (2)° for the lateral and central rings, respectively, compared with 3.6 (2) and 4.2 (2)° in the α-form.

The crystal packing of the two forms is quite different, with a herring-bone type of arrangement in the α-form (Fig. 2) and a π–π type of stacking in the γ-form. In the latter, the molecules form a nearly planar network held together by two types of intermolecular hydrogen bonds: C—H···O through the methoxy groups, with H···O 2.49 Å, and C—H···N through the pyrazine rings, with H···N 2.50 Å (Fig. 3). The stacking distance between these pseudoplanes is 3.40 Å, calculated between a pyrazine centroid in one plane and a nearest neighbour C=C bond in the next. In the α-form, there are also intermolecular interactions of the type C—H···N (H···N 2.58 Å), in this case linking pyrazine rings to phenyl H atoms. Also in the crystal of (I), the phenyl and pyrazine rings of neighbouring molecules are found aligned face to face, suggesting the possible presence of quadrupole–quadrupole interactions.

The most striking result of this work is the evidence found for intermolecular hydrogen bonding through the pyrazine and methoxy groups, and the different roles it plays in the crystal packing and degree of torsion of the conjugated backbone in the two polymorphs.
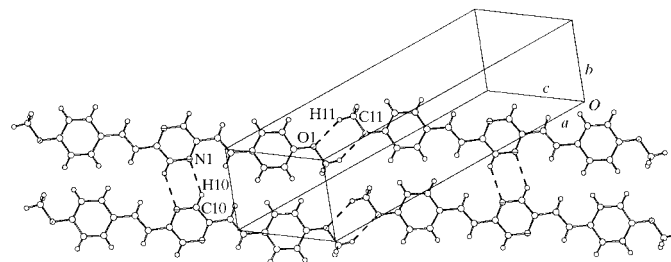

Figure 3
The nearly planar network in the γ-form of (I), showing the C—H···O and C—H···N interactions (H···O 2.49 Å and H···N 2.50 Å). The π–π stacking distance between these pseudoplanes is 3.40 Å.

Experimental

The synthesis of compound (I) is described elsewhere by Grimsdale *et al.* (1997). The γ-form was obtained as thick yellow blocks by slow evaporation of solvent at 278 K from a solution of (I) in CH₂Cl₂. Fast evaporation of solvent from the same solution at 298 K yielded very thin green needles of the α-form. The synchrotron data were collected at the Daresbury SRS, England, on Station 9.8 (Greaves *et al.*, 1997; Clegg *et al.*, 1998).

Compound (I), α form

Crystal data

$C_{22}H_{20}N_2O_2$	Synchrotron radiation
$M_r = 344.40$	$\lambda = 0.68910$ Å
Orthorhombic, *Pccn*	Cell parameters from 5802
$a = 9.1240$ (10) Å	reflections
$b = 26.061$ (3) Å	$\theta = 3.14$–$29.32°$
$c = 7.3280$ (10) Å	$\mu = 0.085$ mm^{-1}
$V = 1742.5$ (4) Å^3	$T = 150$ (2) K
$Z = 4$	Needle, green
$D_x = 1.313$ Mg m^{-3}	$0.18 \times 0.04 \times 0.01$ mm

Data collection

Bruker SMART CCD diffract-ometer	2502 independent reflections
	1979 reflections with $I > 2\sigma(I)$
Thin slice ω-scans	$R_{int} = 0.035$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	$\theta_{max} = 29.44°$
	$h = -12 \rightarrow 7$
$T_{min} = 0.985$, $T_{max} = 0.998$	$k = -36 \rightarrow 36$
9157 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 0.8532P]$
$wR(F^2) = 0.138$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.120$	$(\Delta/\sigma)_{max} = 0.007$
2502 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
119 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H-atom parameters constrained	

Compound (I), γ form

Crystal data

$C_{22}H_{20}N_2O_2$
$M_r = 344.40$
Monoclinic, $C2/c$
$a = 32.339\ (6)$ Å
$b = 5.7320\ (10)$ Å
$c = 9.411\ (2)$ Å
$\beta = 102.815\ (4)°$
$V = 1701.0\ (6)$ Å^3
$Z = 4$
$D_x = 1.345$ Mg m^{-3}

Synchrotron radiation
$\lambda = 0.68910$ Å
Cell parameters from 4261
  reflections
$\theta = 3.64–29.33°$
$\mu = 0.087$ mm^{-1}
$T = 150\ (2)$ K
Block, yellow
$0.14 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART CCD diffract-
  ometer
Thin slice ω-scans
Absorption correction: multi-scan
  (SADABS; Sheldrick, 1997)
  $T_{min} = 0.988$, $T_{max} = 0.991$
5705 measured reflections

2384 independent reflections
1937 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 29.43°$
$h = -43 \rightarrow 45$
$k = -8 \rightarrow 5$
$l = -13 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.141$
$S = 1.089$
2384 reflections
119 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0801P)^2$
  $+ 0.6111P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

H atoms were placed geometrically, with Csp^2—H 0.95 Å and Csp^3—H 0.98 Å, and refined riding on their respective carrier atoms with U_{iso}(H) = 1.2U_{eq}(C). The program *PLATON* (Spek, 1990) was used to calculate the hydrogen-bonding interactions using C—H distances normalized to the neutron-derived value of 1.08 Å.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *LSCELL* (Clegg, 1995); data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SCHAKAL*97 (Keller, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990).

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