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N-Benzyl-2,5-bis(2-thienyl)pyrrole

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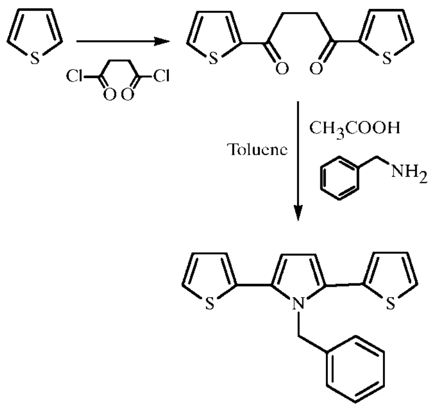
The solid-state structure of the title compound, $C_{19}H_{15}NS_2$, is unusual among substituted thiophene/pyrrole derivatives in that the molecular packing is dominated by π–π interactions between the benzyl substituents. This may be due to the large torsion angles observed between adjacent heterocycles. Torsion angles between adjacent rings in polypyrrole and polythiophene conducting polymers are related to conjugation length and the conductivity properties of the polymer materials. The title compound crystallizes in space group $P2_1/c$ with two molecules in the asymmetric unit, both of which exhibit disorder in one of their thiophene rings.

Comment

We are interested in substituted mixed thiophene/pyrrole oligomers as precursors to substituted conducting polymer materials. These materials are of interest as conducting coatings in a range of emergent technologies, including electronic components, electromagnetic screening, sensors and displays.



(I)

Although not in itself new, the title compound, (I), exemplifies the Paal–Knorr condensation reaction of a parent dione with a substituted amine. In common with several other research groups (Meeker *et al.*, 1998; von Kieseritzky *et al.*, 2002; Raimundo *et al.*, 2000; Ferraris *et al.*, 1989), we have found this route convenient for the preparation of 'trimeric' thiophene–pyrrole–thiophene derivatives substituted at the N atom of the pyrrole ring. This strategy yields centrosymmetric polymer precursors and seeks to minimize the steric influence of the central substituent through the addition of the thiophene spacers.

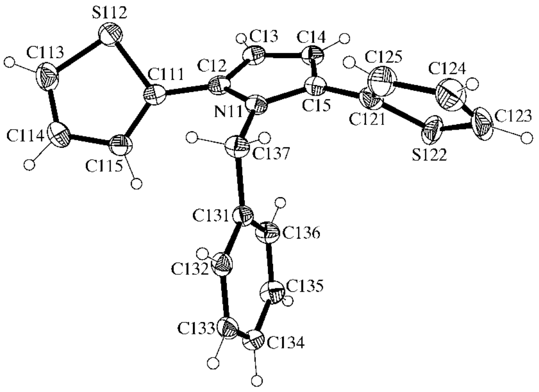


Figure 1
One of the independent molecules of (I) (that containing atoms N11, S112 and S122), shown with 50% probability displacement ellipsoids. The minor disorder component has been omitted.

The asymmetric unit of the crystal structure contains two molecules of (I), shown in Figs. 1 and 2, with different orientations of the substituent thiophene rings. In both molecules, the pendant benzene ring of the benzyl group lies in a plane that is almost perpendicular to the plane of the central pyrrole ring. Although the individual heterocyclic rings are essentially planar, the two outer thiophene rings are twisted with respect to the plane of the pyrrole ring. The magnitude of this twisting is not the same for the two independent molecules, such that the S112—C111—C12—N11 and N11—C15—C121—S122 torsion angles are 130.50 (15) and 128.1 (2)°, respectively, and S222—C221—C25—N21 and N21—C22—C211—S212 are −132.44 (17) and −142.31 (15)°, respectively. These twists are considerably larger than those in *N*-methyl-2,5-bis(2-thienyl)pyrrole, a similar species with a methyl substituent on the N atom of the pyrrole ring (Ferraris *et al.*, 1989), which has values

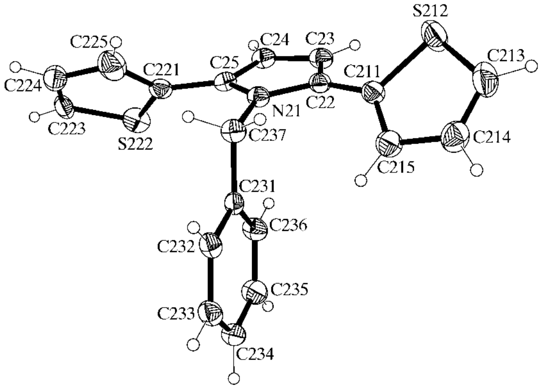


Figure 2
The second independent molecule of (I) (that containing atoms N21, S212 and S222), shown with 50% probability displacement ellipsoids. The minor disorder component has been omitted.

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of −148.9° for S—C—C—N and 151.8° for N—C—C—S. This is consistent with other observations for substituted oligomers of thiophene (Barbarella *et al.*, 1999; Destri *et al.*, 1998; Liao *et al.*, 1994) and phenyl-substituted derivatives of thiophene–pyrrole–thiophene trimers, similar to (I) (Ogura *et al.*, 1999), where increasing the size and proximity of the substituents results in more pronounced torsional twisting. On the other hand, the crystal structure of unsubstituted oligomers of thiophene, for example hexathiophene (Horowitz *et al.*, 1995), shows the rings to be coplanar.

The molecules of (I) are arranged in layers such that along both axes of each layer the benzyl substituent is orientated alternately above and below the plane of the layer (Fig. 3). The phenyl rings in each row of molecules are all coplanar and the equivalent planes in adjacent rows are parallel. Each layer is populated solely by one of the two molecular configurations observed in the asymmetric unit, such that one layer consists of molecules containing atoms S112 and S122, while the adjacent layer is made up of molecules containing atoms S212 and S222. There is a π–π facial interaction between the phenyl rings of the benzyl substituents in adjacent layers. The corresponding C···C distance between cofacial phenyl rings is 3.80 Å. This compares with a distance of 3.39 Å for the layer spacing of graphite. This packing arrangement is also shown schematically in Fig. 4. There is also twofold rotational disorder of one of the thiophene rings in each molecule. Atoms C121 and C221 are common to each of the two disorder components, the occupancies of which refine to 0.553 (3):0.447 (3) and 0.690 (3):0.310 (3), respectively.

This packing arrangement is quite different from those commonly seen in other derivatives and oligomers of thiophene and pyrrole, where an alternating herring-bone motif is often observed (Horowitz *et al.*, 1995; Liao *et al.*, 1994; Destri *et al.*, 1998; Chen *et al.*, 2002). Indeed, when the phenyl ring interaction is absent, for example in *N*-methyl-2,5-bis(2-thienyl)pyrrole, this type of packing arrangement is adopted (Ferraris *et al.*, 1989). In phenyl derivatives of the dithienylpyrrole moiety (see, for example, Ogura *et al.*, 1999), a packing arrangement is observed which is quite similar to that reported here. However, in that case, the phenyl rings are much further apart. In both the phenyl derivatives and the benzyl derivative reported here, the torsion angles between the adjacent heterocycles of the molecule are quite large. Presumably this will render the packing interactions between neighbouring dithienylpyrrole units less favourable compared with molecular geometries in which this backbone moiety is planar.

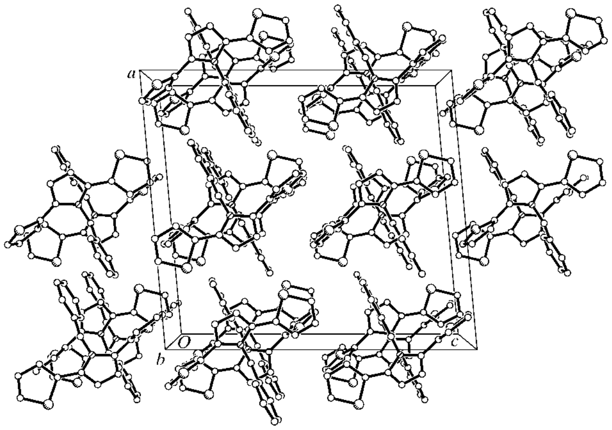

Figure 3
A packing diagram of (I), viewed along *b*, with phenyl rings edge-on going alternately into and out of the *ac* plane.

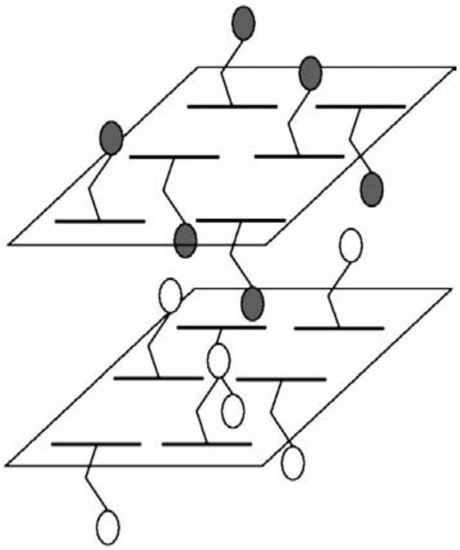

Figure 4
A schematic representation of the packing of (I), showing the phenyl ring of the substituent as a pendant ellipse. Two adjacent layers are shown, shaded differently for clarity.

Experimental

The title compound was prepared by the Paal–Knorr ring-closure reaction of 1,4-bis(2-thienyl)butane-1,4-dione with benzylamine (see scheme). The syntheses of both species have been described previously (*e.g.* Just *et al.*, 2002), but for completeness, we include here improved experimental details of the ring-closure reaction. The procedure detailed below gives a much higher yield, together with better purity, than that described by Just *et al.* (2002). A 100 ml round-bottomed flask was charged with 1,4-bis(2-thienyl)butane-1,4-dione (1.1 g, 4.4 mmol), toluene (50 ml) and glacial acetic acid (5 ml). Benzylamine (1.85 g, 17 mmol) was added dropwise to this solution. The flask was equipped with a Dean–Stark apparatus and the reaction was stirred under reflux overnight, with constant removal of water by azeotropic distillation. The reaction mixture was concentrated *in vacuo* and the residue dissolved in dichloromethane. This solution was washed with aqueous sodium bicarbonate and saturated aqueous sodium chloride. The organic solution was dried over $MgSO_4$ and the solvent removed *in vacuo*. The brown solid was purified using silica-gel chromatography with hexane–dichloromethane (3:1) as eluant, affording (I) in 88% yield as a white solid, which was crystallized from hot hexane as colourless crystals. Spectroscopic analysis, ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, δ): 5.29 (2H, *s*, CH_2), 6.39 (2H, *s*), 6.70 (2H, *dd*, J = 1.2 Hz and 3.6 Hz), 6.83 (2H, *dd*, J = 3.6 Hz and 5.0 Hz), 6.88 (2H, *m*, ArH), 7.10 (2H, *dd*, J = 1.2 Hz and 5.0 Hz), 7.20 (3H, *m*, ArH).

Crystal data

$C_{19}H_{15}NS_2$
$M_r = 321.44$
Monoclinic, $P2_1/c$
$a = 16.8050\ (8)$ Å
$b = 10.0004\ (5)$ Å
$c = 18.6253\ (9)$ Å
$\beta = 95.241\ (2)^\circ$
$V = 3117.0\ (3)$ Å^3
$Z = 8$
$D_x = 1.37$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9139 reflections
$\theta = 2.2$–29.0°
$\mu = 0.34$ mm^{-1}
$T = 150\ (2)$ K
Block, colourless
$0.68 \times 0.35 \times 0.16$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.803$, $T_{\max} = 0.948$
26 998 measured reflections
7546 independent reflections
5517 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 29.0^\circ$
$h = -22 \rightarrow 22$
$k = -13 \rightarrow 13$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.134$
$S = 1.04$
7546 reflections
471 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 1.513P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

H atoms were placed in geometrically calculated positions (with aryl C—H distances of 0.95 Å and aliphatic C—H distances of 0.99 Å) and refined using a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Positional disorder (twofold ring rotation about common atoms C121 and C221) was modelled with restraints to geometric and anisotropic displacement parameters, giving refined occupancies of 0.553 (3) for atoms S122/C123–C125, 0.447 (3) for S127/C128–C130, 0.690 (3) for S222/C223–C225 and 0.310 (3) for S227/C228–C230.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program used to solve structure: *SHELXTL* (Sheldrick, 2001); program used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1552). Services for accessing these data are described at the back of the journal.

References

Barbarella, G., Zambianchi, M., Antolini, L., Ostoja, P., Maccagnani, P., Bongini, A., Marseglia, E. A., Tedesco, E., Gigli, G. & Cingolani, R. (1999). *J. Am. Chem. Soc.* **121**, 8920–8926.

Bruker (2001). *SMART* (Version 5.611) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, Y., Harrison, W. T. A., Imrie, C. T. & Ryder, K. S. (2002). *J. Mater. Chem.* **12**, 579–585.

Destri, S., Ferro, D. R., Khotina, I. A., Porzio, W. & Farina, A. (1998). *Macromol. Chem. Phys.* **199**, 1973–1979.

Ferraris, J. P., Andrus, R. G. & Hrncir, D. C. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1318–1320.

Horowitz, G., Bachet, B., Yassar, A., Lang, P., Demanze, F., Fave, J.-L. & Garnier, F. (1995). *Chem. Mater.* **7**, 1337–1341.

Just, P. E., Chane-Ching, K. I. & Lacaze, P. C. (2002). *Tetrahedron*, **58**, 3467–3472.

Kieseritzky, F. von, Hellberg, J., Wang, X. J. & Inganas, O. (2002). *Synthesis*, **9**, 1195–1200.

Liao, J.-H., Benz, M., LeGoff, E. & Kanatzidis, M. G. (1994). *Adv. Mater.* **6**, 135–138.

Meeker, D. L., Mudigonda, D. S. K., Osborn, J. M., Loveday, D. C. & Ferraris, J. P. (1998). *Macromolecules*, **31**, 2943–2946.

Ogura, K., Yanai, H., Miokawa, M. & Akazome, M. (1999). *Tetrahedron Lett.* **40**, 8887–8891.

Raimundo, J.-M., Blanchard, P., Brisset, H., Akoudad, S. & Roncali, J. (2000). *Chem. Commun.* pp. 939–940.

Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2003). *SADABS*. Version 2.08. University of Göttingen, Germany.