2,5-Bis(4-nitrophenyl)-3,4-diphenylthiophene

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Abstract. $C_{28}H_{18}N_2O_4S$, $M_r = 478.52$, orthorhombic, *Pbcn*, $a = 24.507$ (4), $b = 10.945$ (2), $c = 8.835$ (1) Å, $V = 2369.8$ (7) Å^3, $Z = 4$, $D_x = 1.341$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.66$ cm^{-1}, $F(000) = 992$, $T = 295$ K. Final $R = 0.040$ for 980 observed reflections. The structure shows that the 4-nitrophenyl groups are attached to positions 2 and 5 of the thiophene ring selectively. The bond distances in the thiophene ring are: S—C, 1.724 (3); C=C, 1.381 (4) and C—C, 1.429 (3) Å and the angle C—S—C is 93.0 (1)°.

Introduction. A number of reactions between aryl and alkyl diisocyanates with glycols leading to the formation of polyurethanes have been reported (Lenz, 1967; Smith, 1963; Burkus & Eckert, 1958). Recently, 2,5-bis(4-isocyanatophenyl)-3,4-diphenylthiophene (I) has been synthesized (Maldar & Hosmane, 1986) in our laboratory from 2,5-bis(4-nitrophenyl)-3,4-diphenylthiophene (II) which is a bright-yellow air-stable solid. The preparation of this dinitro derivative (II) has been described elsewhere (Dilthey & Graef, 1938).

(II)
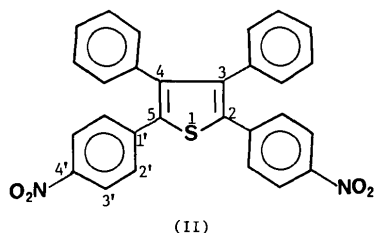
The diamino derivative of (II) has been allowed to react with aromatic dianhydrides, dialdehydes and diacid chlorides to yield polyimides, polyazomethines and polyamides, respectively (Imai, Maldar & Kakimoto, 1984, 1985; Kakimoto, Negi & Imai, 1985). For example, the polycondensation of diamine H$_2$N—R—NH$_2$ with diacid chloride Cl(O)C—R'—C(O)Cl yields the polyamide –{R—NH—CO—R'—CO—NH}–$_n$. Our recent ^{1}H and ^{13}C NMR investigations suggested that the 4-nitrophenyl group is attached to the thiophene ring preferentially at positions 2 and 5. In

order to confirm this selectivity and to provide definitive characterization of (I) and (II), we have conducted an X-ray investigation of the title compound (II) and report herein the results.

Experimental. Crystals of the title compound are yellow rectangular plates. Unit-cell parameters by least-squares fit of 15 reflections in range $11 < 2\theta < 22°$, space group *Pbcn* from systematic absences (0*kl*, *k* odd; *h*0*l*, *l* odd and *hk*0, *h + k* odd). Crystals 0.55 × 0.29 × 0.15 mm, automatic Syntex *P*2$_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\theta/2\theta$ scanning mode, 1564 independent reflections in range $3 < 2\theta < 45°$, *hkl* range $h\,0\rightarrow26$, $k\,0\rightarrow11$, $l\,0\rightarrow9$, 980 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics, three standard reflections remeasured every 100 reflections showed a random variation of less than 3% in intensity, Lorentz–polarization correction, no absorption correction, direct-methods *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refinement by full-matrix least squares using *SHELX*76 (Sheldrick, 1976), anisotropic, H atoms located in difference Fourier maps, isotropic temperature factors for H, $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0.040$, $wR = 0.033$. Two strong low-angle reflections 202 and 302, possibly affected by extinction with $\Delta F = -30$ and -21 respectively, were taken out during the final refinement. $(\Delta/\sigma)_{max} = 0.19$, max. height in final difference Fourier map 0.19 e Å^{-3}. Atomic scattering factors for C, H, O, N and S and the effects of the anomalous-dispersion correction for S used were those stored in *SHELX*76.

Discussion. The final atomic parameters are given in Table 1.† The identification of the atoms and the configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1. The molecule lies on a diad axis which passes through the S atom and the center of the C(2)—C(2') bond. The bond lengths, bond

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† Lists of structure factors, anisotropic thermal parameters and deviations from least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42601 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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angles, and selected torsion angles with their standard deviations are given in Table 2. The geometry of the thiophene ring is in good agreement with the data obtained for thiophene by electron diffraction (Harshbarger & Bauer, 1970). The C—S and C=C distances of 1·724 (3) and 1·381 (4) Å are similar to the average distances of 1·717 (4) and 1·368 (4) Å found for the same bonds in thiophene. The angle between the phenyl and thiophene rings is −72·0 (1)° while that between the nitrophenyl and thiophene rings is 26·6 (1)°. The angle between the nitro group and the phenyl ring to which it is attached is 1·0 (5)°.

Table 1. Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-H and isotropic for H atoms (e.s.d.'s in parentheses)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
S	½	0·8937 (1)	¼	0·0577 (3)*
C(1)	0·5477 (1)	1·0021 (3)	0·3003 (3)	0·0474 (8)
C(2)	0·5273 (1)	1·1184 (2)	0·2784 (3)	0·0437 (7)
C(3)	0·6010 (1)	0·9607 (2)	0·3578 (3)	0·0482 (8)
C(4)	0·6311 (1)	1·0317 (3)	0·4571 (4)	0·0559 (10)
C(5)	0·6811 (1)	0·9941 (4)	0·5127 (4)	0·0628 (10)
C(6)	0·7008 (1)	0·8833 (3)	0·4691 (4)	0·0604 (10)
C(7)	0·6731 (1)	0·8087 (3)	0·3714 (4)	0·0641 (10)
C(8)	0·6231 (1)	0·8473 (3)	0·3176 (4)	0·0605 (10)
N(1)	0·7534 (1)	0·8410 (3)	0·5321 (4)	0·0836 (10)
O(1)	0·7769 (1)	0·9090 (2)	0·6186 (3)	0·1147 (10)
O(2)	0·7697 (1)	0·7436 (3)	0·4932 (4)	0·1435 (12)
C(9)	0·5578 (1)	1·2330 (2)	0·3085 (3)	0·0456 (8)
C(10)	0·5408 (2)	1·3149 (3)	0·4179 (4)	0·0616 (11)
C(11)	0·5698 (2)	1·4203 (3)	0·4454 (5)	0·0830 (14)
C(12)	0·6152 (2)	1·4462 (4)	0·3608 (6)	0·0886 (15)
C(13)	0·6324 (2)	1·3685 (4)	0·2514 (5)	0·0833 (12)
C(14)	0·6034 (1)	1·2625 (3)	0·2248 (4)	0·0623 (10)
H(4)	0·618 (1)	1·111 (3)	0·485 (2)	0·036 (8)
H(5)	0·702 (1)	1·051 (2)	0·588 (3)	0·079 (12)
H(7)	0·688 (1)	0·731 (3)	0·336 (3)	0·086 (12)
H(8)	0·603 (1)	0·802 (2)	0·257 (3)	0·033 (8)
H(10)	0·510 (1)	1·299 (2)	0·469 (3)	0·043 (10)
H(11)	0·558 (1)	1·467 (3)	0·522 (3)	0·080 (13)
H(12)	0·637 (1)	1·520 (3)	0·380 (4)	0·117 (15)
H(13)	0·667 (1)	1·381 (3)	0·174 (4)	0·130 (15)
H(14)	0·615 (1)	1·208 (2)	0·146 (3)	0·048 (9)

* The standard deviations of U_{eq}'s were calculated according to Schomaker & Marsh (1983).
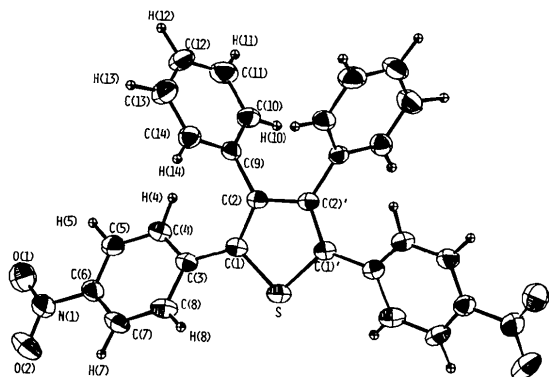

Fig. 1. *ORTEP* drawing of the molecule. Thermal ellipsoids scaled to enclose 50% probability. H atoms are represented as spheres of arbitrary radii.

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°) with e.s.d.'s in parentheses

S—C(1)	1·724 (3)	C(6)—N(1)	1·478 (4)
C(1)—C(2)	1·381 (4)	C(7)—C(8)	1·381 (4)
C(1)—C(3)	1·473 (4)	N(1)—O(1)	1·212 (4)
C(2)—C(2ⁱ)	1·429 (3)	N(1)—O(2)	1·189 (4)
C(2)—C(9)	1·484 (3)	C(9)—C(10)	1·383 (5)
C(3)—C(4)	1·385 (4)	C(9)—C(14)	1·378 (4)
C(3)—C(8)	1·400 (4)	C(10)—C(11)	1·377 (6)
C(4)—C(5)	1·383 (5)	C(11)—C(12)	1·370 (6)
C(5)—C(6)	1·361 (5)	C(12)—C(13)	1·355 (7)
C(6)—C(7)	1·368 (4)	C(13)—C(14)	1·381 (6)
C(1)—S—C(1ⁱ)	93·0 (1)	C(7)—C(6)—N(1)	118·9 (3)
S—C(1)—C(2)	110·7 (2)	C(6)—C(7)—C(8)	118·4 (3)
S—C(1)—C(3)	118·6 (2)	C(3)—C(8)—C(7)	121·8 (3)
C(2)—C(1)—C(3)	130·8 (2)	C(6)—N(1)—O(1)	117·3 (3)
C(1)—C(2)—C(2ⁱ)	112·8 (2)	C(6)—N(1)—O(2)	117·7 (3)
C(1)—C(2)—C(9)	124·9 (2)	O(1)—N(1)—O(2)	125·0 (3)
C(2ⁱ)—C(2)—C(9)	122·3 (2)	C(2)—C(9)—C(10)	121·4 (3)
C(1)—C(3)—C(4)	121·2 (2)	C(2)—C(9)—C(14)	120·7 (2)
C(1)—C(3)—C(8)	121·9 (2)	C(10)—C(9)—C(14)	117·9 (3)
C(4)—C(3)—C(8)	116·9 (2)	C(9)—C(10)—C(11)	120·7 (4)
C(3)—C(4)—C(5)	122·0 (3)	C(10)—C(11)—C(12)	119·8 (4)
C(4)—C(5)—C(6)	118·6 (3)	C(11)—C(12)—C(13)	120·8 (4)
C(5)—C(6)—C(7)	122·3 (3)	C(12)—C(13)—C(14)	119·3 (4)
C(5)—C(6)—N(1)	118·8 (3)	C(9)—C(14)—C(13)	121·5 (3)
C(2)—C(1)—C(3)—C(4)	27·6 (6)	C(1)—C(2)—C(9)—C(10)	−116·3 (5)
C(2)—C(1)—C(3)—C(8)	−153·7 (4)	C(2ⁱ)—C(2)—C(9)—C(14)	−114·2 (4)
S—C(1)—C(3)—C(8)	26·7 (5)	C(2ⁱ)—C(2)—C(9)—C(10)	64·1 (5)
S—C(1)—C(3)—C(4)	−152·0 (4)	C(3)—C(1)—C(2)—C(9)	1·1 (6)
C(1)—C(2)—C(9)—C(14)	65·4 (5)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

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