# 3,4-Dinitro-N,N,N′,N′-tetraphenylthiophene-2,5-diamine

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The title compound, $C_{28}H_{20}N_4O_4S$, studied with X-ray crystallography, NMR, mass spectrometry and elemental analysis, is presented. The two C=C double bonds are slightly shorter than those of the parent thiophene, while the C—C single bond is slightly elongated.

Comment

The title compound, (I), has been shown to be an excellent precursor for the production of low-band-gap conjugated polymers and organic light-emitting devices (OLEDs) (Thomas et al., 2002). Standard procedures including bromination, nitration and a palladium-catalysed aromatic C—N coupling reaction were used to synthesize the donor–π-acceptor-type compound, (I), in high yield (see scheme). The compound is soluble in organic solvents and was purified by column chromatography.
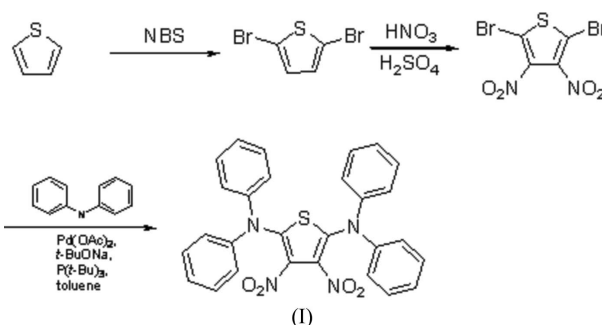
The dihedral angles between the thiophene (S/C2–C5) and benzene rings (C11–C16, C21–C26, C31–36 and C41–46) are 87.16(6), 79.81(6), 74.49(6) and 72.81(6)°, respectively, and that between the two benzene rings (C11–C16 and C21–C26, C31–36 and C41–46) are 59.98(7) and 74.77(7)°. The structure can be regarded as consisting of alternating (010) layers. The double bonds of (I) are shorter [C2—C3 = 1.353 (3) Å] than those of the parent thiophene [C2—C3 = 1.370 (2) Å], while the C—C single bond is slightly elongated [C3—C4 = 1.425 (3) Å] compared with the parent thiophene [C3—C4 = 1.423 (2) Å] (Bak et al., 1961). This bond localization in (I) can be attributed to the donor–π-acceptor nature of the substituents, as well as steric repulsion between the two NO_2 groups.

Experimental

A two-necked round-bottomed flask was charged with Pd(OAc)₂ (0.023 g, 1 mmol), t-BuONa (1.15 g, 1.2 mmol), 2,5-dibromo-3,4-dinitrothiophene (1.66 g, 5 mmol) and diphenylamine (1.68 g, 10 mmol). Dry toluene was added and the reaction mixture was

stirred under nitrogen for 10 min. Tri-*tert*-butylphosphine (2 mmol%) in dry toluene was added through a syringe (1.0 mmol of the phosphine in 1 ml of dry toluene). The reaction mixture was heated at 363 K for 20 h. After cooling, the mixture was diluted with diethyl ether and the organic phase was washed with water and brine. After drying over anhydrous $MgSO_4$ and removing the volatiles, the residue was purified by column chromatography using CH_2Cl_2/*n*-hexane as eluent, followed by recrystallization from CH_2Cl_2 and MeOH. Crystals suitable for single-crystal X-ray diffraction were grown from a CH_2Cl_2 solution layered with hexane at room temperature. The compound was obtained as a red solid in 79% yield. FAB MS: m/e 509 $(M+H)^+$; ^1H NMR (CDCl$_3$): δ 7.09 (d, J = 7.7 Hz, 8H, *ortho*-C$_6$H$_5$), 7.15 (t, J = 7.3 Hz, 4H, *para*-C$_6$H$_5$), 7.31 (t, J = 7.7 Hz, 8H, *meta*-C$_6$H$_5$). Analysis calculated for $C_{28}H_{20}N_4O_4S$: C 66.13, H 3.96, N 11.02%; found: C 66.35, H 3.67, N 11.42%.

Crystal data

$C_{28}H_{20}N_4O_4S$	$D_x = 1.397$ Mg m^{-3}
$M_r = 508.54$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3556
$a = 9.9075$ (4) Å	reflections
$b = 19.0621$ (7) Å	$\theta = 2.2$–24.7°
$c = 13.5418$ (5) Å	$\mu = 0.18$ mm^{-1}
$\beta = 108.977$ (2)°	$T = 100$ (2) K
$V = 2418.47$ (16) Å^3	Prism, red
$Z = 4$	$0.34 \times 0.2 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	3379 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.035$
Absorption correction: none	$\theta_{max} = 25.0°$
22681 measured reflections	$h = -11 \rightarrow 11$
4264 independent reflections	$k = -22 \rightarrow 22$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 1.644P]$
$wR(F^2) = 0.101$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
4264 reflections	$\Delta\rho_{max} = 0.92$ e Å^{-3}
335 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	

H atoms were positioned geometrically and treated as riding atoms, with C—H = 0.95–0.98 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).
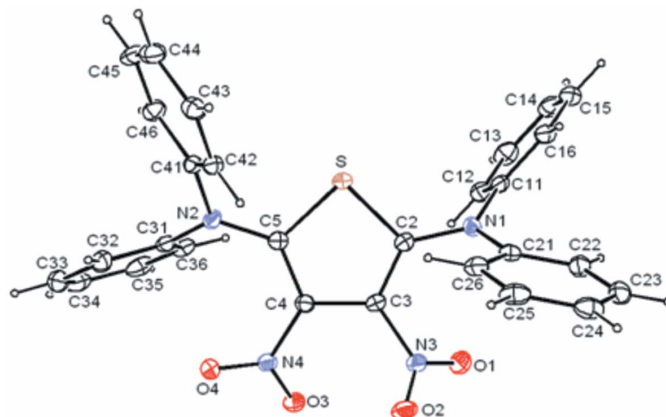
Figure 1
The molecular structure of (I), drawn with 30% probability displacement ellipsoids, showing the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.
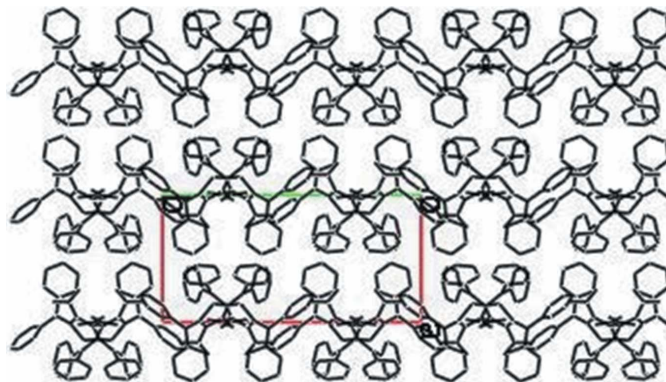

Figure 2
Packing diagram for (I), viewed along the *c* axis. H atoms have been omitted for clarity.

References

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