2,8-Bis(diphenylamino)-5H-5λ^6-dibenzo[b,d]-thiophene 5,5-dioxide

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In the title compound, $C_{36}H_{26}N_2O_2S$, the two benzene rings fused to the thiophene ring form a dihedral angle of 8.78 (8)°. In the crystal structure, there are no significant hydrogen-bonding interactions or π–π stacking interactions between molecules.

Comment

The application of organic electroluminescent devices (OELD) in flat-panel displays using small organic molecules or organic polymers has been intensively pursued following the reports by the Kodak team (Tang *et al.*, 1987) and the Cambridge group (Burroughes *et al.*, 1990). The title compound, (I), was synthesized by the condensation of a dione (scheme) with diphenylamine and it can be used as an *n*-type OELD (Huang *et al.*, 2006). The molecular structure is shown in Fig. 1.
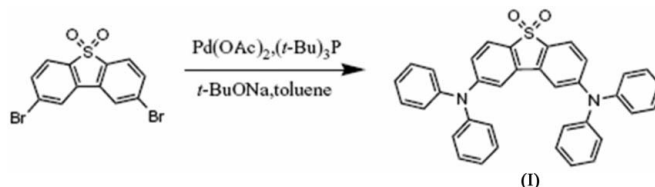
The dihedral angles between the plane of the dibenzo-thiophene S,S-dioxide ($P$1) and the four terminal phenyl rings ($P$2, $P$3, $P$4 and $P$5; see Fig. 1 for ring definitions) are 83.15 (8), 55.49 (8), 51.60 (8) and 64.35 (8)°, respectively. The dihedral angles are 72.21 (8) and 70.35 (8)° for $P$2/$P$3 and$P$4/$P$5, respectively.

Experimental

A two-necked round-bottomed flask was charged with Pd(OAc)$_2$ (1 mmol% per halogen atom), *t*-BuONa (1.2 equivalents per halogen atom), 2,8-dibromo-5,5-dioxo-5H-5λ^6-dibenzothiophene (5 mmol), and diphenylamine (2 equivalents per halogen atom). Dry toluene (50 ml) was added and the mixture was stirred under nitrogen for 10 min. Tri-*tert*-butylphosphine (2 mmol%) in dry toluene was added *via* a syringe (the stock solution contained 1.0 mmol of the phosphine in 1 ml of dry toluene). The reaction mixture was heated at 353 K for 16 h. After cooling, the mixture was diluted with diethyl ether and the organic phase was washed with water and brine. After drying over MgSO$_4$ and removal of the volatiles, the residue was purified by column chromatography using ethyl acetate/hexanes (1:9) as eluant, followed by recrystallization from CH$_2$Cl$_2$ and MeOH (2:1). The compound was obtained as a pale-yellow solid in 53% yield. ^{1}H NMR (CDCl$_3$): δ 6.97 (*dd*, 2H, J_1 = 8.5 Hz, J_2 = 2.0 Hz, C$_6$H$_3$), 7.06–7.12 (*m*, 14H, C$_6$H$_3$, *ortho*-, *para*-C$_6$H$_5$), 7.24–7.29 (*m*, 8H, *meta*-C$_6$H$_5$), 7.55 (*d*,

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2H, J = 8.5 Hz, C_6H_3). FAB MS (m/e): 550 (M^+) Analysis calculated for $C_{36}H_{26}N_2O_2S$: C 78.52, H 4.76, N 5.09%; found: C 78.09, H 4.42, N 5.12%.

Crystal data

$C_{36}H_{26}N_2O_2S$
M_r = 550.65
Monoclinic, $P2_1/n$
a = 9.8988 (2) Å
b = 19.3898 (4) Å
c = 14.4606 (3) Å
β = 93.866 (1)°
V = 2769.19 (10) Å^3
Z = 4
D_x = 1.321 Mg m^{-3}

D_m measured by not measured
Mo $K\alpha$ radiation
Cell parameters from 6419 reflections
θ = 2.6–30.9°
μ = 0.15 mm^{-1}
T = 100 (1) K
Prism, yellow
0.3 × 0.22 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
40230 measured reflections
4880 independent reflections

4135 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.0°
h = −11 → 11
k = −23 → 23
l = −17 → 17

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.092
S = 1.04
4880 reflections
371 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 1.6477P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.0015 (4)

H atoms were positioned geometrically and refined as riding, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(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:
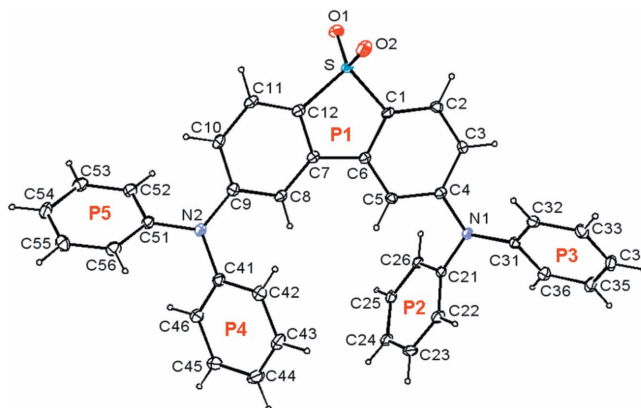

Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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