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The crystal structure of ethyl 5-(4-(diphenylamino)phenyl)thiophene-2-carboxylate, $C_{25}H_{21}NO_2S$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.18 mm ⁻¹
Diffractometer:	XtaLAB Synergy
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13285, 3681, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2942
$N(\text{param})_{\text{refined}}$:	263
Programs:	CrysAlis ^{PRO} [1], SHELX [2]

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Abstract

$C_{25}H_{21}NO_2S$, monoclinic, $P2_1/n$ (no. 14), $a = 8.21802(18)$ Å, $b = 7.42687(17)$ Å, $c = 34.2757(8)$ Å, $\beta = 91.149(2)^\circ$, $V = 2091.57(8)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0388$, $wR_{\text{ref}}(F^2) = 0.1337$, $T = 293(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared by the reported method [3], using 5-[4-(diphenylamino)phenyl]thiophene-2-carbaldehyde (1.065 g, 3 mmol), $KMnO_4$ (1.896 g, 12 mmol) and K_2CO_3 (0.275 g, 2 mmol) in 50 mL acetone/ H_2O ($v:v = 2:1$). The mixture was refluxed for 4 h. The solution was adjusted to pH = 1 with HCl, and then filtered. The crude intermediate 5-(4-(diphenylamino)phenyl)thiophene-2-carboxylic acid

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.1191(2)	0.8767(3)	0.17529(5)	0.0530(5)
C2	−0.2218(3)	1.0077(3)	0.18991(6)	0.0644(5)
H2	−0.3336	0.9984	0.1856	0.077*
C3	−0.1592(3)	1.1518(3)	0.21075(7)	0.0757(6)
H3	−0.2295	1.2370	0.2210	0.091*
C4	0.0053(3)	1.1706(3)	0.21655(7)	0.0804(7)
H4	0.0468	1.2683	0.2305	0.096*
C5	0.1078(3)	1.0442(4)	0.20162(7)	0.0789(7)
H5	0.2197	1.0578	0.2050	0.095*
C6	0.0471(2)	0.8961(3)	0.18151(6)	0.0651(6)
H6	0.1181	0.8095	0.1722	0.078*
C7	−0.3339(2)	0.6493(3)	0.16628(6)	0.0544(5)
C8	−0.4508(3)	0.6040(3)	0.13850(7)	0.0692(6)
H8	−0.4309	0.6221	0.1122	0.083*
C9	−0.5983(3)	0.5312(3)	0.14989(10)	0.0906(8)
H9	−0.6770	0.5008	0.1311	0.109*
C10	−0.6282(3)	0.5043(4)	0.18826(12)	0.1029(10)
H10	−0.7271	0.4558	0.1958	0.123*
C11	−0.5128(4)	0.5483(4)	0.21580(10)	0.1025(9)
H11	−0.5337	0.5297	0.2421	0.123*
C12	−0.3660(3)	0.6201(4)	0.20511(7)	0.0769(7)
H12	−0.2880	0.6489	0.2241	0.092*
C13	−0.0960(2)	0.6437(3)	0.12436(5)	0.0529(5)
C14	−0.0161(2)	0.7467(3)	0.09673(5)	0.0546(5)
H14	−0.0192	0.8717	0.0983	0.066*
C15	0.0672(2)	0.6656(3)	0.06713(5)	0.0519(5)
H15	0.1209	0.7369	0.0492	0.062*
C16	0.0731(2)	0.4784(2)	0.06346(5)	0.0460(4)
C17	−0.0079(2)	0.3771(3)	0.09095(6)	0.0562(5)
H17	−0.0070	0.2522	0.0891	0.067*
C18	−0.0900(2)	0.4578(3)	0.12110(6)	0.0602(5)
H18	−0.1418	0.3866	0.1394	0.072*
C19	0.1638(2)	0.3943(2)	0.03167(5)	0.0479(4)
C20	0.2671(3)	0.4742(3)	0.00616(6)	0.0616(5)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H20	0.2893	0.5970	0.0063	0.074*
C21	0.3364(2)	0.3536(3)	−0.02015(6)	0.0604(5)
H21	0.4091	0.3880	−0.0392	0.072*
C22	0.2866(2)	0.1812(2)	−0.01493(5)	0.0508(4)
C23	0.3263(2)	0.0187(3)	−0.03657(6)	0.0554(5)
C24	0.4781(3)	−0.1061(3)	−0.08792(7)	0.0725(6)
H24A	0.3848	−0.1501	−0.1029	0.087*
H24B	0.5174	−0.2021	−0.0710	0.087*
C25	0.6088(3)	−0.0478(3)	−0.11466(7)	0.0784(7)
H25A	0.5699	0.0501	−0.1306	0.118*
H25B	0.6386	−0.1468	−0.1311	0.118*
H25C	0.7021	−0.0093	−0.0996	0.118*
N1	−0.1834(2)	0.7260(2)	0.15492(5)	0.0619(4)
O1	0.2691(2)	−0.1271(2)	−0.03041(6)	0.0883(5)
O2	0.43238(17)	0.04888(18)	−0.06487(4)	0.0643(4)
S1	0.14951(6)	0.16688(6)	0.022171(14)	0.05573(19)

was recrystallized from anhydrous ethanol. The intermediate acid was dissolved in 20 mL miscible liquids (ethanol and H₂SO₄). The mixture was refluxed for 8 h. After the mixture was cooled to room temperature, the most ethanol was removed. The residue was dispersed into 20 mL of water. The solution was adjusted to pH = 8 with K₂CO₃ and extracted three times with CH₂Cl₂. The mixture was purified by silica gel chromatography column using petroleum/ethylacetate (10:1 v/v) as the eluent. A light yellow solid product was collected. The yellow crystals of the title compound were obtained on slow evaporation of the CH₃CN solvent.

Experimental details

All H-atoms were placed in calculated positions and treated as riding: C–H = 0.93–0.97 Å, with *U*_{iso}(H) = 1.2 or 1.5 *U*_{eq} (parent C-atom).

Comment

Triphenylamine is a very popular building block for the construction of application in electroluminescent devices, solid-state lasers, and nonlinear optical devices, resulting from its propeller-shaped structure. This system has multiple advantages (such as electron donating ability, excellent hole transporting, tridimensional steric and good light

harvesting properties) and there are several syntheses of its derivatives [3–6].

There is one molecule in the asymmetric unit (see the Figure). The dihedral angles between the mean planes of the phenyl rings in triphenylamine are 64.1(2)°, 107.5(2)° and 151.1(1)°, respectively. The angles around N1 are 120.96(15)°, 119.96(15)° and 119.01(15)°. The dihedral angle between the mean plane of the thiophene and its connecting the phenyl ring is 10.1(1)°. Moreover, the ester group is only twisted by 2.4(3)° with respect to the thiophene unit (see the Figure). Geometric parameters are in the expected ranges [7].

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