Crystal structure of *N,N,N',N'*-tetra-*m*-tolyl-anthracene-9,10-diamine, $C_{42}H_{36}N_2$

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Abstract

$C_{42}H_{36}N_2$, monoclinic, $P12_1/c1$ (no. 14),
 $a = 8.279(3)$ Å, $b = 16.998(6)$ Å, $c = 11.812(4)$ Å,
 $\beta = 93.599(7)^\circ$, $V = 1659.0$ Å³, $Z = 2$,
 $R_{\text{gt}}(F) = 0.068$, $wR_{\text{ref}}(F^2) = 0.161$, $T = 295$ K.

Source of material

To a 25 ml sidearm flask in a nitrogen box was added 9,10-dibromoanthracene (1.25 mmol), di-*m*-tolyl-amine (2.50 mmol), $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.025 mmol, $\text{Pd}/\text{Br} = 1\%$), tri-*tert*-butylphosphine (0.03 mmol), and sodium *tert*-butoxide (3.0 mmol). The flask was sealed with septum and then moved out of the nitrogen box. To the flask was injected via a syringe *o*-xylene (10 ml). The reaction mixture was heated and stirred at 120 °C under nitrogen for an appropriate time until the reaction was complete. The reaction mixture was then cooled to room temperature, filtered through a mixture of celite and silica gel pad and washed with dichloromethane. The filtrate was washed with water and then dried by MgSO_4 . Concentration of the filtrate on a rotary evaporator followed by washing of the solid material with methanol afforded the desired crude product. The crude product was then dried at 120 °C in a vacuum and was further purified by sublimation. Orange crystals of the title compound were obtained by sublimation at $(4\text{--}6) \times 10^{-3}$ Pa for 16 h.

Experimental details

All H atoms except methyl hydrogen atoms were found in the difference Fourier map and refined freely. H atoms of the methyl groups were treated at calculated positions with C–H distances of 0.96 Å.

Discussion

The arylamine moiety is a structural component in a variety of synthesis and naturally occurring biologically active compounds [1]. Triarylamines are standard hole transport materials [2–4], many synthetic methods for the construction of an aryl-nitrogen bond have been reported [5–10]. The modest yields of copper-mediated reaction, that is conventionally used to prepare triarylamine, limit size and topology of this material [5]. Palladium complexes are effective catalysts for the cross-coupling of aryl halides and amines in the presence of sodium *tert*-butoxide [6–10]. But the crystal structure of *N,N,N',N'*-tetra-*m*-tolyl-anthracene-9,10-diamine has not been reported in past papers. In the structure, the molecule is located in the centre of symmetry. The carbon atoms of the anthracene ring are fully coplanar. The atoms C1, N1, C8, and C14 are also coplanar and angles of C1–N1–C14, C1–N1–C8, and C8–N1–C14 are nearly 120°. The angle between two tolyl groups attached on the nitrogen atom is 62.9(1)°, so that the compound has little steric crowding. It is worth noting that the molecule likes a chair-shape. Further modification of this kind of molecule could lead to more interesting molecule architectures.

Table 1. Data collection and handling.

Crystal:	orange, columnar, size $0.38 \times 0.38 \times 0.50$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.66 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\text{max}}$:	50.2°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8556, 2944
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2243
$N(\text{param})_{\text{refined}}$:	199
Programs:	SHELX-97 [11], Ortep-3 [12], WinGX [13]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(20A)	4e	0.4645	0.8800	0.2812	0.153
H(20B)	4e	0.2754	0.8824	0.2825	0.153
H(20C)	4e	0.3574	0.8484	0.1769	0.153
H(21A)	4e	-0.4821	0.5790	0.1996	0.103
H(21B)	4e	-0.4941	0.5352	0.0825	0.103
H(21C)	4e	-0.5049	0.6272	0.0866	0.103
H(4A)	4e	0.0242	0.3041	0.5541	0.050
H(5A)	4e	0.1400	0.2466	0.3984	0.050
H(6A)	4e	0.2044	0.3259	0.2372	0.050

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(7A)	4e	0.1649	0.4643	0.2466	0.050
H(9A)	4e	0.3558	0.5673	0.4427	0.050
H(10A)	4e	0.5651	0.6584	0.4934	0.050
H(11A)	4e	0.5809	0.7780	0.4023	0.050
H(13A)	4e	0.1405	0.7393	0.2337	0.050
H(15A)	4e	0.1786	0.6106	0.1091	0.050
H(16A)	4e	0.0132	0.6018	-0.0599	0.050
H(17A)	4e	-0.2660	0.5895	-0.0546	0.050
H(19A)	4e	-0.2244	0.5898	0.2845	0.050

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(1)	4e	0.0905(3)	0.5980(1)	0.3187(2)	0.043(1)	0.038(1)	0.034(1)	-0.008(1)	-0.0030(9)	0.0059(9)
C(1)	4e	0.0440(3)	0.5486(1)	0.4102(2)	0.032(1)	0.038(1)	0.032(1)	-0.006(1)	-0.003(1)	0.006(1)
C(2)	4e	0.0672(3)	0.4667(1)	0.4028(2)	0.034(1)	0.034(1)	0.034(1)	-0.002(1)	-0.003(1)	0.002(1)
C(3)	4e	0.0225(3)	0.4168(1)	0.4953(2)	0.034(1)	0.031(1)	0.036(1)	-0.003(1)	-0.003(1)	0.002(1)
C(4)	4e	0.0527(3)	0.3334(1)	0.4873(2)	0.047(2)	0.033(1)	0.041(2)	-0.002(1)	-0.002(1)	0.001(1)
C(5)	4e	0.1211(3)	0.3023(2)	0.3959(2)	0.055(2)	0.032(1)	0.055(2)	0.002(1)	-0.002(1)	-0.007(1)
C(6)	4e	0.1642(4)	0.3511(2)	0.3058(2)	0.058(2)	0.048(2)	0.045(2)	0.004(1)	0.006(1)	-0.010(1)
C(7)	4e	0.1393(3)	0.4303(2)	0.3093(2)	0.052(2)	0.043(2)	0.038(2)	0.002(1)	0.006(1)	-0.000(1)
C(8)	4e	0.2286(3)	0.6471(2)	0.3381(2)	0.041(2)	0.048(2)	0.035(1)	-0.009(1)	0.003(1)	0.001(1)
C(9)	4e	0.3567(4)	0.6220(2)	0.4114(3)	0.051(2)	0.072(2)	0.050(2)	-0.014(2)	-0.005(1)	0.015(2)
C(10)	4e	0.4888(4)	0.6709(3)	0.4337(3)	0.054(2)	0.122(3)	0.061(2)	-0.033(2)	-0.015(2)	0.015(2)
C(11)	4e	0.4942(5)	0.7447(3)	0.3841(3)	0.070(2)	0.107(3)	0.065(2)	-0.055(2)	0.000(2)	-0.004(2)
C(12)	4e	0.3672(4)	0.7712(2)	0.3112(3)	0.069(2)	0.062(2)	0.061(2)	-0.030(2)	0.014(2)	-0.001(2)
C(13)	4e	0.2349(4)	0.7216(2)	0.2885(2)	0.055(2)	0.046(2)	0.049(2)	-0.013(1)	0.004(1)	0.003(1)
C(14)	4e	-0.0074(3)	0.5980(1)	0.2150(2)	0.043(2)	0.025(1)	0.034(1)	-0.003(1)	-0.001(1)	0.003(1)
C(15)	4e	0.0615(3)	0.6035(2)	0.1103(2)	0.045(2)	0.044(2)	0.041(2)	0.001(1)	0.006(1)	0.000(1)
C(16)	4e	-0.0356(3)	0.6002(2)	0.0113(2)	0.056(2)	0.053(2)	0.032(1)	0.008(1)	0.004(1)	-0.002(1)
C(17)	4e	-0.2018(4)	0.5916(2)	0.0134(2)	0.058(2)	0.045(2)	0.036(2)	0.005(1)	-0.009(1)	-0.006(1)
C(18)	4e	-0.2734(3)	0.5870(2)	0.1165(2)	0.045(2)	0.037(2)	0.050(2)	-0.001(1)	-0.004(1)	-0.001(1)
C(19)	4e	-0.1741(3)	0.5898(2)	0.2164(2)	0.045(2)	0.042(2)	0.035(1)	-0.004(1)	0.004(1)	0.003(1)
C(20)	4e	0.3660(6)	0.8531(2)	0.2580(4)	0.121(4)	0.066(2)	0.122(4)	-0.047(2)	0.021(3)	0.007(2)
C(21)	4e	-0.4553(4)	0.5816(2)	0.1218(3)	0.048(2)	0.090(3)	0.066(2)	-0.006(2)	-0.011(2)	-0.001(2)

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