Crystal structure of *N,N,N',N'*-tetraphenyl-1,4-benzenediamine, $C_{30}H_{24}N_2$

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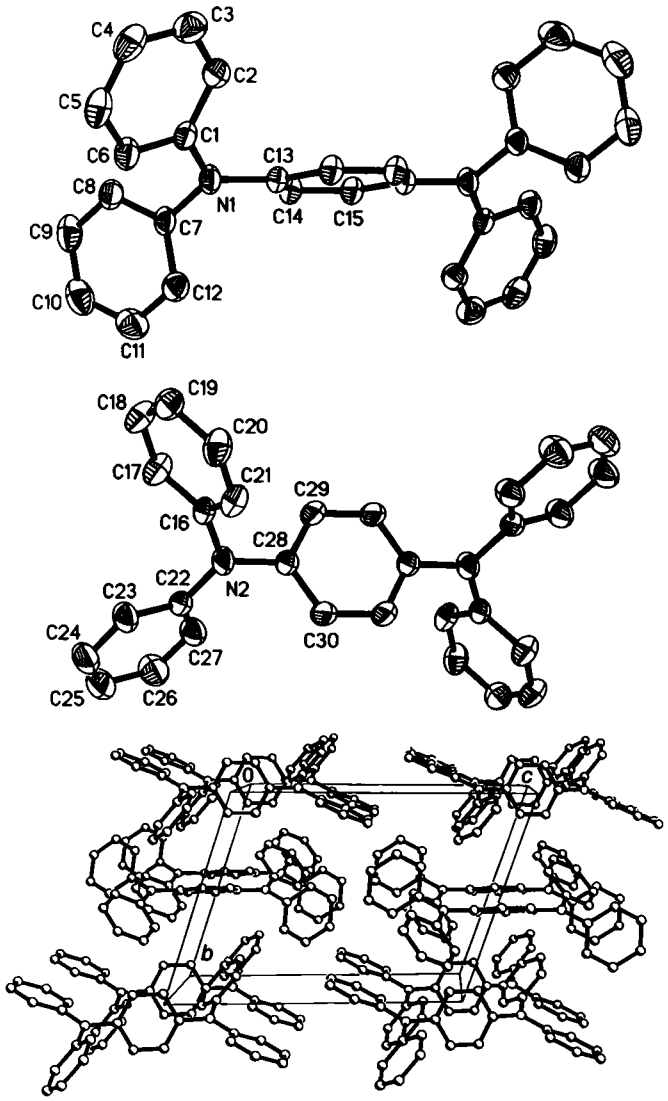

Abstract

$C_{30}H_{24}N_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.435(2)$ Å, $b = 10.410(1)$ Å, $c = 13.802(2)$ Å, $\alpha = 106.37(1)°$, $\beta = 99.84(2)°$, $\gamma = 96.04(2)°$, $V = 1130.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.050$, $wR_{ref}(F^2) = 0.132$, $T = 293$ K.

Source of material

Triphenylamine (1.0 g, 4.08 mmol) was dissolved in benzene (50 ml) and methanesulfonic acid (CH_3SO_3H, 0.5 ml) was added. The mixture was refluxed for 5 hours with stirring under argon atmosphere. After benzene was distilled, the residue was column-chromatographed on silica gel (60-90 °C, eluent: petroleum ether) to afford title compound in ca. 5 % yield. Single crystals suitable for X-ray analysis were obtained by slow evaporation from an ethyl acetate solution at room temperature.

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Experimental details

Although the crystal had rather poor quality and the N_{gt}/N_{param} ratio has been low, all hydrogen atoms were found from Fourier difference maps and were refined freely.

Discussion

Triphenylamine and its derivatives are of interest as hole transporting materials for electroluminescent devices due to their ability to be vacuum deposited and high hole drift mobilities [1,2]. Furthermore, knowledge of intermolecular interactions is necessary to understand the solid-state electronic and transport properties. We present here the structure of *N,N,N',N'*-tetraphenyl-1,4-benzenediamine.

The title compound crystallizes centrosymmetrically with two half molecules in the asymmetric unit. The important dimensions of the two molecules do not differ significantly, and they are typical for other similar structures [3-7]. The two molecules take up a symmetry propeller-like shape, all the C–N–C' angles are almost equal to 120° and all the N—C bonds spread almost symmetrically from the N1 or N2 atoms. This means that the N1 and N2 atom are sp^2 hybridized and the lone electron pair is involved in conjugation with phenyl moieties. The average N—C bonds (mean 1.423 Å) are ca. 0.010 Å longer than in aromatic amines and ca. 0.046 Å shorter than in aliphatic ones [8].

Table 1. Data collection and handling.

Crystal:	white prism, size 0.11 × 0.34 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.71 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	55.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6498, 5402
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2197
$N(param)_{refined}$:	386
Program:	SHELXTL [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.194(2)	0.319(2)	0.056(1)	0.054(6)
H(3)	2*i*	−0.065(3)	0.245(2)	0.075(2)	0.078(8)
H(4)	2*i*	−0.152(3)	0.327(2)	0.230(2)	0.083(8)
H(5)	2*i*	0.027(3)	0.498(2)	0.367(2)	0.076(8)
H(6)	2*i*	0.286(2)	0.578(2)	0.346(2)	0.065(7)
H(8)	2*i*	0.511(2)	0.387(2)	0.326(1)	0.057(6)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9)	2*i*	0.711(3)	0.471(3)	0.482(2)	0.097(9)
H(10)	2*i*	0.866(3)	0.684(3)	0.524(2)	0.11(1)
H(11)	2*i*	0.814(3)	0.821(3)	0.413(2)	0.10(1)
H(12)	2*i*	0.611(2)	0.737(2)	0.262(2)	0.063(7)
H(14)	2*i*	0.692(2)	0.462(2)	0.130(1)	0.059(6)
H(15)	2*i*	0.237(2)	0.542(2)	0.025(1)	0.049(6)
H(17)	2*i*	0.299(3)	−0.196(3)	0.252(2)	0.10(1)
H(18)	2*i*	0.035(3)	−0.299(3)	0.233(2)	0.100(9)
H(19)	2*i*	−0.186(3)	−0.219(3)	0.151(2)	0.094(9)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(20)	2*i*	−0.130(3)	−0.038(2)	0.088(2)	0.087(9)
H(21)	2*i*	0.147(3)	0.063(2)	0.111(2)	0.089(8)
H(23)	2*i*	0.351(3)	0.093(3)	0.375(2)	0.098(9)
H(24)	2*i*	0.541(3)	0.181(2)	0.529(2)	0.094(9)
H(25)	2*i*	0.824(3)	0.182(3)	0.535(2)	0.11(1)
H(26)	2*i*	0.910(3)	0.113(2)	0.378(2)	0.079(8)
H(27)	2*i*	0.725(3)	0.031(2)	0.226(2)	0.087(8)
H(29)	2*i*	0.399(3)	−0.208(2)	0.023(2)	0.082(7)
H(30)	2*i*	0.527(3)	0.204(2)	0.131(2)	0.072(7)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.2608(3)	0.4565(2)	0.2006(2)	0.050(1)	0.057(1)	0.043(1)	0.006(1)	0.014(1)	0.025(1)
C(2)	2*i*	0.1566(3)	0.3552(2)	0.1210(2)	0.058(2)	0.063(2)	0.052(1)	0.001(1)	0.016(1)	0.017(1)
C(3)	2*i*	0.0030(3)	0.3093(3)	0.1327(2)	0.058(2)	0.074(2)	0.078(2)	−0.003(2)	0.010(2)	0.030(2)
C(4)	2*i*	−0.0466(3)	0.3589(3)	0.2232(2)	0.051(2)	0.093(2)	0.090(2)	0.012(2)	0.023(2)	0.054(2)
C(5)	2*i*	0.0557(3)	0.4589(3)	0.3024(2)	0.066(2)	0.095(2)	0.063(2)	0.023(2)	0.032(2)	0.040(2)
C(6)	2*i*	0.2081(3)	0.5086(3)	0.2919(2)	0.058(2)	0.074(2)	0.048(1)	0.007(1)	0.017(1)	0.025(1)
C(7)	2*i*	0.5450(3)	0.5567(2)	0.2827(2)	0.050(1)	0.067(2)	0.038(1)	0.003(1)	0.016(1)	0.019(1)
C(8)	2*i*	0.5756(3)	0.4775(3)	0.3475(2)	0.065(2)	0.075(2)	0.050(1)	0.002(2)	0.012(1)	0.026(1)
C(9)	2*i*	0.6937(3)	0.5273(4)	0.4366(2)	0.066(2)	0.120(3)	0.055(2)	0.012(2)	0.007(1)	0.040(2)
C(10)	2*i*	0.7838(4)	0.6538(4)	0.4616(2)	0.063(2)	0.122(3)	0.054(2)	0.001(2)	0.004(2)	0.017(2)
C(11)	2*i*	0.7564(3)	0.7314(3)	0.3974(2)	0.059(2)	0.087(2)	0.073(2)	−0.011(2)	0.013(2)	0.009(2)
C(12)	2*i*	0.6365(3)	0.6836(3)	0.3077(2)	0.056(2)	0.071(2)	0.055(2)	0.001(1)	0.016(1)	0.021(1)
C(13)	2*i*	0.4582(3)	0.5031(2)	0.0946(1)	0.054(1)	0.052(1)	0.036(1)	0.004(1)	0.013(1)	0.0184(9)
C(14)	2*i*	0.6114(3)	0.4804(2)	0.0774(2)	0.048(1)	0.060(2)	0.045(1)	0.010(1)	0.011(1)	0.026(1)
C(15)	2*i*	0.3474(3)	0.5237(2)	0.0161(2)	0.047(1)	0.061(2)	0.045(1)	0.011(1)	0.014(1)	0.023(1)
C(16)	2*i*	0.2472(3)	−0.0578(2)	0.1809(2)	0.056(2)	0.062(2)	0.043(1)	0.003(1)	0.021(1)	0.018(1)
C(17)	2*i*	0.2142(3)	−0.1649(3)	0.2188(2)	0.058(2)	0.085(2)	0.086(2)	0.012(2)	0.021(2)	0.051(2)
C(18)	2*i*	0.0541(4)	−0.2235(3)	0.2071(2)	0.069(2)	0.080(2)	0.096(2)	0.003(2)	0.031(2)	0.047(2)
C(19)	2*i*	−0.0720(4)	−0.1781(3)	0.1584(2)	0.056(2)	0.086(2)	0.068(2)	0.002(2)	0.025(1)	0.024(2)
C(20)	2*i*	−0.0399(3)	−0.0725(3)	0.1210(2)	0.060(2)	0.102(2)	0.071(2)	0.025(2)	0.028(1)	0.042(2)
C(21)	2*i*	0.1185(3)	−0.0125(3)	0.1326(2)	0.072(2)	0.070(2)	0.070(2)	0.016(2)	0.031(1)	0.036(1)
C(22)	2*i*	0.5217(3)	0.0545(2)	0.2831(2)	0.059(2)	0.057(2)	0.047(1)	−0.004(1)	0.019(1)	0.013(1)
C(23)	2*i*	0.4686(4)	0.0992(3)	0.3746(2)	0.073(2)	0.091(2)	0.052(2)	−0.002(2)	0.025(2)	0.010(1)
C(24)	2*i*	0.5812(4)	0.1477(3)	0.4670(2)	0.095(2)	0.104(2)	0.052(2)	−0.010(2)	0.026(2)	0.002(2)
C(25)	2*i*	0.7444(4)	0.1552(3)	0.4709(2)	0.084(2)	0.111(3)	0.061(2)	−0.014(2)	0.000(2)	0.014(2)
C(26)	2*i*	0.7961(4)	0.1121(3)	0.3805(2)	0.067(2)	0.109(3)	0.075(2)	0.001(2)	0.016(2)	0.015(2)
C(27)	2*i*	0.6875(3)	0.0630(3)	0.2876(2)	0.067(2)	0.083(2)	0.055(2)	0.002(2)	0.022(2)	0.009(1)
C(28)	2*i*	0.4574(3)	0.0020(2)	0.0935(2)	0.059(2)	0.065(2)	0.044(1)	−0.007(1)	0.019(1)	0.014(1)
C(29)	2*i*	0.4389(3)	−0.1181(3)	0.0156(2)	0.084(2)	0.057(2)	0.058(1)	−0.010(1)	0.028(1)	0.017(1)
C(30)	2*i*	0.5175(3)	0.1208(3)	0.0771(2)	0.082(2)	0.055(2)	0.053(1)	−0.010(1)	0.029(1)	0.006(1)
N(1)	2*i*	0.4191(2)	0.5067(2)	0.1916(1)	0.051(1)	0.076(1)	0.0354(9)	−0.005(1)	0.0104(9)	0.0213(9)
N(2)	2*i*	0.4101(2)	0.0021(2)	0.1881(1)	0.062(1)	0.098(2)	0.042(1)	−0.016(1)	0.019(1)	0.019(1)

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