

N-(3-Methylphenyl)-*N,N*-bis(4-methylphenyl)amineTouraj Manifar,^a Sohrab Rohani^a
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Key indicators

Single-crystal X-ray study

 $T = 295$ KMean $\sigma(\text{C}-\text{C}) = 0.006$ Å R factor = 0.071 wR factor = 0.245

Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $\text{C}_{21}\text{H}_{21}\text{N}$, crystallizes in space group $P\bar{1}$, with $Z = 6$. The N atom is sp^2 -hybridized. The geometry of each of the three independent molecules is unremarkable. The interaction of the three molecules is discussed.

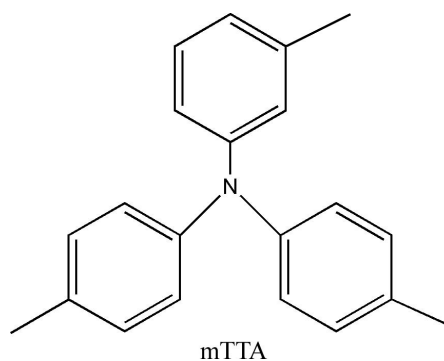
Comment

Arylamine molecules are characterized as an important class of hole transport materials because of their high drift mobility (Brantly *et al.*, 1971; Brantly *et al.*, 1972; Klupfel *et al.*, 1965). They have numerous industrial applications such as multilayer systems for photocopying devices (Borsenberger & Wiess, 1998), white light electro-luminescent devices (Strukelj, 1996), low-cost flat panel displays (Bulovic *et al.*, 1996), and voltage-tunable color organic LEDs (Kaliowski, 1999). These materials are utilized in the solid state and the desirable intermolecular electron transfer is highly dependent on the crystallographic characteristics of these molecules (Kennedy *et al.*, 2002). The nature and number of intermolecular contacts as well as the conformation of the central fragment of the molecule are crucial characteristics (Manifar *et al.*, 2005).

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In this study, the crystal structure analysis of *N*-(3-methylphenyl)-*N,N*-bis(4-methylphenyl)amine, hereafter referred to as mTTA, is reported. This investigation was carried out as part of a comprehensive study on the solubility and purification of the arylamine class of molecules. mTTA showed a strong resistance toward crystallization. Thus, it may be considered a potential hole transfer material since one of the degradation pathways in organic LEDs is crystallization upon ageing (Manifar *et al.*, 2004).

There are three unique molecules of mTTA in the asymmetric unit. One of the molecules is represented in Fig. 1. The geometry of all three molecules is similar (Table 1) and in all cases the N atom is sp^2 hybridized. The real differences between the three molecules are found in how they pack. The N10 species has two face-to-face interactions, one with each of

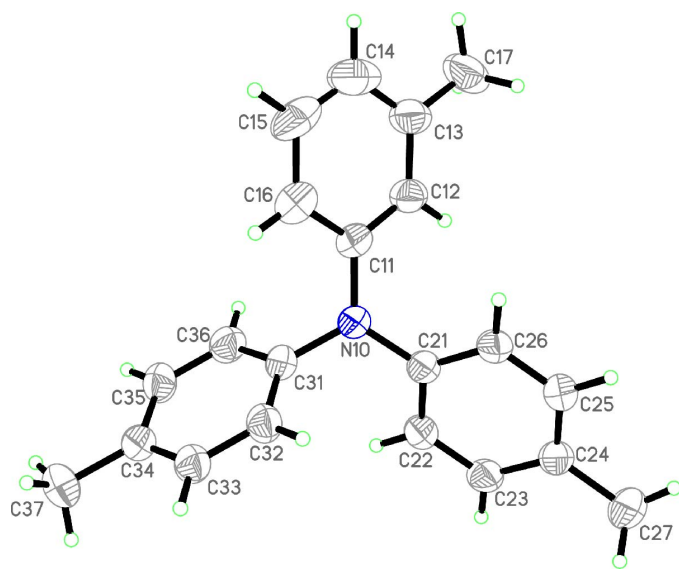


Figure 1

The structure of one molecule of the asymmetric unit of mTTA, showing 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by circles of arbitrary size.

the other two (N40 and N70) species (Fig. 2). The remaining two rings of both N40 and N70 have only edge-to-face interactions with their nearest neighbours.

Two *para*-methyl aromatic rings have a face-to-face interaction with a closest contact of 3.706 (4) Å (C25...C97). The dihedral angle between the two planes is 5.0 (3)°. The *meta*-methyl aromatic ring of N10 forms a face-to-face interaction with the *meta*-methyl ring of N40. The dihedral angle is 10.2 (3)° and the closest contact is 3.602 (4) Å (C14...C47). Both face-to-face interactions are in a head-to-tail arrangement with regards to the methyl group.

Experimental

mTTA was prepared according to our ligated copper catalyst method. A 500 ml four-necked round-bottomed flask was fitted with an argon inlet, standard thermometer, mechanical stirrer and a Dean-Stark trap/condenser. To this flask were added 4-iodotoluene (100 g, 0.458 mol), *m*-toluidine (17.48 g, 0.163 mol), potassium hydroxide (110 g, 1.96 mol), copper(I) bromide (1.16 g, 0.008 mol), a ligand (2,2'-bipyridyl, 0.008 mol) and decane as solvent (100 g). The mixture was allowed to reflux under argon. High-performance liquid chromatography (HPLC) verified the completion of the reaction. Upon observing reaction completion, the organic portion obtained was diluted with toluene and then treated with a mixture of acidic alumina and acid-leached bentonite at 353 K for 2 h. The solution was hot-filtered and the resulting mixture was evaporated under reduced pressure. The resulting liquid was diluted with methanol (2 l) and heated to boiling, yielding a clear solution. After cooling to 277 K over the course of 24 h, a soft gummy material was formed. A further 24 h of cooling resulted in hard crystals. The crystals were separated by filtration and purity was verified by HPLC. Single crystals of mTTA were grown from a saturated solution of HPLC grade *n*-hexane in a 50 ml vial covered with perforated parafilm. X-ray quality single crystals appeared over the course of a month at 273–274 K (m.p. 329.7 K).

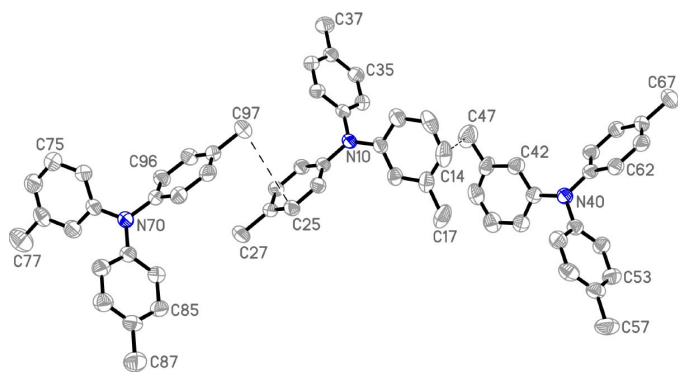


Figure 2

Diagram of three unique molecules of mTTA and their interactions (dashed lines). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

Crystal data

C₂₁H₂₁N
M_r = 287.39
 Triclinic, *P* $\bar{1}$
a = 11.1573 (6) Å
b = 14.8063 (12) Å
c = 16.8629 (13) Å
 α = 66.738 (3)°
 β = 86.740 (4)°
 γ = 83.251 (4)°
V = 2541.4 (3) Å³

Z = 6
D_x = 1.127 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 10662 reflections
 θ = 1.7–25.0°
 μ = 0.07 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.28 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
T_{min} = 0.985, *T_{max}* = 0.995
 24267 measured reflections
 8908 independent reflections

3216 reflections with *I* > 2σ(*I*)
R_{int} = 0.074
 θ_{max} = 25.0°
h = -13 → 13
k = -15 → 17
l = -20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.071
wR(*F*²) = 0.245
S = 0.93
 8908 reflections
 596 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.118P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL*
 Extinction coefficient: 0.0094 (16)

Table 1

Selected geometric parameters (Å, °).

N10—C11	1.407 (4)	N70—C91	1.431 (4)
N10—C21	1.430 (4)	N40—C41	1.419 (5)
N10—C31	1.433 (4)	N40—C61	1.420 (4)
N70—C71	1.421 (4)	N40—C51	1.435 (4)
N70—C81	1.430 (4)		
C11—N10—C21	123.3 (3)	C81—N70—C91	120.1 (3)
C11—N10—C31	118.5 (3)	C41—N40—C61	122.3 (3)
C21—N10—C31	118.1 (3)	C41—N40—C51	118.5 (3)
C71—N70—C81	121.2 (3)	C61—N40—C51	116.8 (3)
C71—N70—C91	118.7 (3)		

H atoms were positioned geometrically and constrained as riding atoms, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms and C—H = 0.96 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL/PC*.

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