

N,N,N-Tris(3-methylphenyl)amine

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Key indicators

Single-crystal X-ray study

 $T = 296$ KMean $\sigma(\text{C}-\text{C}) = 0.005$ Å R factor = 0.065 wR factor = 0.220

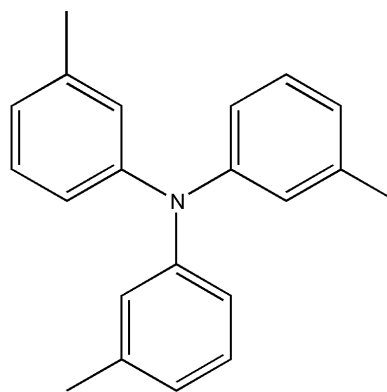
Data-to-parameter ratio = 14.7

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

The crystal structure of the title complex, $\text{C}_{21}\text{H}_{21}\text{N}$, consists of discrete molecules with unremarkable geometry. The N atom is sp^2 -hybridized. Comparisons are made with other arylamine molecules.

Comment

Arylamine molecules form stable aminium radical cations and hence are of great interest for many industrial applications. Xerographics, pharmaceuticals, and agrochemicals are among the industries that benefit from these molecules (Goodbrand & Nan-Xing, 1999; Louie & Hartwig, 1997; Manifar *et al.*, 2004; Manifar & Rohani, 2004; Negwer, 1994).



(I)

In our previous studies, we have investigated the best reaction route for the synthesis of these types of molecules (Manifar *et al.*, 2004). Their electrochemical and solubility properties were examined, and *N,N,N*-tris(3-methylphenyl)amine, hereafter referred to as mmmTTA [shown as (I) in scheme] showed some distinctive characteristics. Its electrochemical properties, as well as its resistance toward crystallization, makes it a good candidate as an organic light-emitting diode (OLED). One of the causes of degradation in OLEDs is the tendency of the hole transport materials to crystallize upon aging (Dodabalapur *et al.*, 1999; Forest *et al.*, 2000; Hosokawa, 1995).

Structural studies of trisaryl-substituted amines are of interest in their own right. The π conjugation between the lone electron pair and the adjoining aromatic systems is the reason for the increased stability of the aminium radical cations. It is this stability that makes them industrially interesting. Therefore, we decided to invest the time in growing an X-ray quality crystal and examining its structure. The molecular structure of mmmTTA is shown in Fig. 1.

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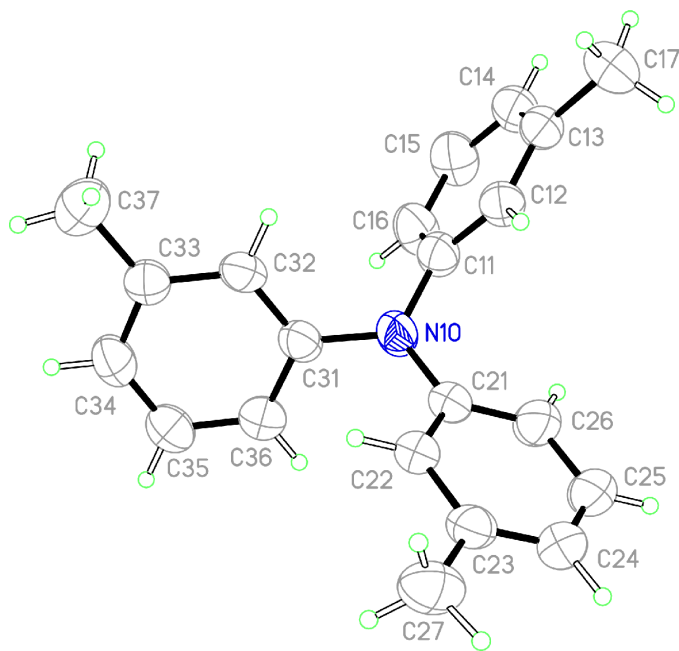


Figure 1
The structure of mmmTTA, showing 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by circles of arbitrary size.

The geometry around the N atom of mmmTTA shows a slightly distorted sp^2 -hybridization. The C–N–C angles are indicative of a planar geometry [119.2 (3), 119.4 (3) and 120.9 (3)°], however, the N atom is displaced by 0.051 (4) Å from the plane of the three C atoms to which it is bonded. The aromatic rings of adjacent mmmTTA molecules nest together in a staggered arrangement.

Each of the aromatic rings is twisted out of the mean plane defined by the N atom and its three bound C atoms. The torsion angles range from 31.2 (5) to 55.8 (5)°. This is unremarkable and can be compared with triphenylamine, 37.0 (7)–50.5 (7)° (Sobolev *et al.*, 1985). Certainly, the increased size of the methylphenyl group in the title complex would give more extreme torsion angles than the analogous phenyl complex. When compared to *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, however, the differences are more noticeable (Kennedy *et al.*, 2002). The torsion angles range from 18.9 (5) to 56.3 (5)° for the 3-methylphenyl compound. The extreme angle of 18.9 (5)° is associated with one end of the biphenyl group. If the lowest torsion angle, 18.9 (5)°, is ignored, then the range of 27.1 (5)–56.3 (5)° is in keeping with the values observed for the other mentioned structures.

Experimental

mmmTTA was synthesized and purified by 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 3-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. Reaction completion was verified by HPLC. Upon observing reaction completion, the resulting 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 viscous liquid was dissolved in methanol and yielded a yellow oil as a stable second liquid phase. Large quantities of methanol were used to dissolve mmmTTA and then the mixture was refluxed at elevated temperatures. After cooling the mixture, gummy crystals formed which, in turn, yielded hard crystals after 1 d in HPLC grade methanol. A saturated solution was prepared in a 50 ml vial with *n*-hexanes. The top was perforated and the vial was kept at 278–279 K for a month. Colourless plates were formed and they were separated by filtration. HPLC confirmed the purity of the product.

Crystal data

$C_{21}H_{21}N$
 $M_r = 287.39$
Orthorhombic, *Pbca*
 $a = 18.8439$ (13) Å
 $b = 16.3922$ (9) Å
 $c = 10.8561$ (7) Å
 $V = 3353.4$ (4) Å³
 $Z = 8$
 $D_x = 1.138$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 15740 reflections
 $\theta = 1.7$ – 26.4°
 $\mu = 0.07$ mm⁻¹
 $T = 296$ (2) K
Plate, colourless
0.38 × 0.25 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995)
 $T_{\min} = 0.837$, $T_{\max} = 1.000$
37114 measured reflections
2947 independent reflections

1238 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.108$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -19 \rightarrow 22$
 $k = -19 \rightarrow 19$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.220$
 $S = 1.00$
2947 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1088P)^2 + 0.0808P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³
Extinction correction:
SHELXTL/PC
Extinction coefficient: 0.0070 (14)

H atoms were positioned geometrically and constrained as riding atoms, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *COLLECT* (Nonius, 1997–2001); 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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