Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N,*N*-Bis-(3-methylphenyl)-*N*-(4-methylphenyl)amine

Touraj Manifar,[a] Sohrab Rohani[a] and Michael, C. Jennings[b]*

[a]Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9, and [b]Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B9

Correspondence e-mail: mjenning@uwo.ca

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.170
Data-to-parameter ratio = 13.9

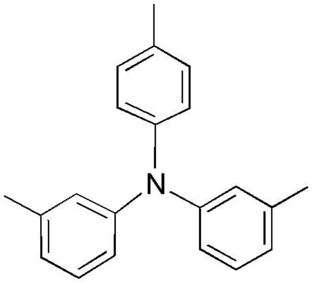
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title complex, $C_{21}H_{21}N$, the molecule lies on a twofold rotation axis. The N atom is sp^2 hybridized. Comparisons are made with similar compounds in this series.

Received 2 March 2005
Accepted 4 April 2005
Online 9 April 2005

Comment

Arylamines are considered an important class of molecules because of their widespread applications. Polymer (Chan *et al.*, 1995), pharmaceutical (Hong *et al.*, 1998) and xerographic companies (Goodbrand & Nan-Xing, 1999) are just some of the industries that have applications for these molecules. High drift mobilities (Brantly *et al.*, 1971, 1972; Klupfel *et al.*, 1965) make these molecules a good choice for OLEDs (organic light-emitting diodes) or as hole-transport materials in organic photoreceptors (Manifar & Rohani, 2004).



(I)

The title compound, (I), is an arylamine with two *meta*-substituted methyl groups and one *para*-substituted methyl group (see scheme). Compound (I) crystallizes in the space group *Pbcn* with four atoms (N10, C11, C14, and C15) lying on the twofold axis (Wykcoff letter *c*, site symmetry 2). The molecular structure of the full molecule is shown in Fig. 1. Compound (I) adopts the expected propeller-like conformation and the bond lengths and angles are normal.

This paper completes the series of arylamines we have been examining. We have studied the physical properties of tritolylamine (TTA), mTTA (one methyl group in the *meta* position), mmTTA [two *meta*-methyl groups, (I); this work], and mmmTTA (three *meta*-methyl groups) (Manifar, Bender *et al.*, 2005). Our studies have shown that the enthalpy of vaporization decreases in the order mTTA > TTA > mmTTA > mmmTTA. This clearly shows that the intermolecular forces between mTTA molecules are the strongest and we postulated that these strong intermolecular forces would be plausibly explained by the solid-state structure. Consequently, we have determined the crystal structures of mTTA (Manifar, Rohani & Jennings, 2005), mmTTA (present work) and mmmTTA

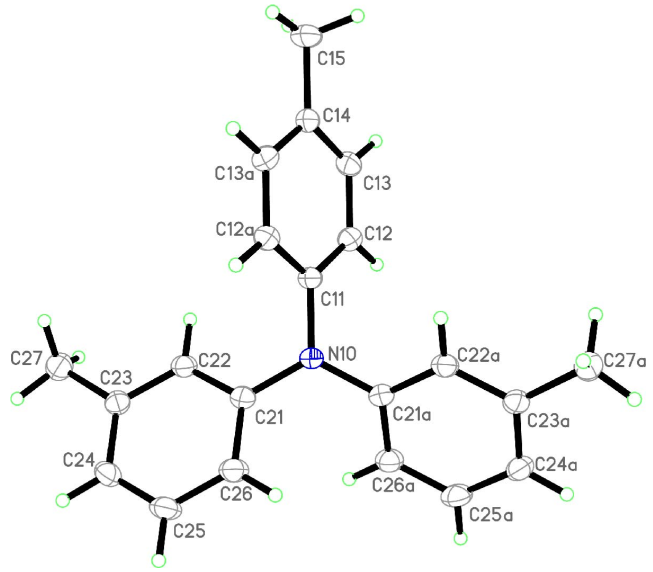


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by circles of arbitrary size. Atoms having labels with suffix a are related by the symmetry operator $1 - x, y, \frac{1}{2} - z$.

(Manifar *et al.*, 2004). The crystal structure of TTA had already been determined by Reynolds & Scaringe (1982).

The bond lengths and angles are similar in all four cases. The differences lie in the interaction of the molecules with their nearest neighbours. Compounds mmmTTA and mmTTA both have the propeller-like molecules interlocking in pairs. Compound mTTA, however, crystallizes with $Z' = 3$. The central molecule forms face-to-face interactions with the aryl groups of the molecules on either side. However, this contact is still mainly governed by van der Waals forces. It is possible that the prevalent methyl-to-methylbenzene face interactions are a factor in the different enthalpies of vaporization. A more in-depth crystal packing analysis is necessary and this is currently being carried out.

Experimental

The preparation of compound (I) was based on our ligated copper catalyst method. A 500 ml four-necked round-bottomed flask was fitted with an argon inlet, a standard thermometer, a mechanical stirrer and a Dean-Stark trap/condenser. To this flask were added 3-iodotoluene (100 g, 0.458 mol), *p*-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′-dipyridyl, 0.008 mol) and decane as solvent (100 g). The mixture was allowed to reflux under argon. The reaction was monitored every 20–30 min by high-performance liquid chromatography (HPLC) until completion. Upon observing reaction completion, the resulting organic portion was diluted in 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 in methanol and heated to boiling, yielding a clear mixture. Upon cooling to 277 K for 24 h, crystals of (I) formed and were separated by filtration. The crystal purity was confirmed by HPLC. A saturated solution of (I) in HPLC grade *n*-hexane was prepared in a 50 ml vial and covered with perforated Parafilm. X-ray quality single crystals of (I) appeared over the course of a month at 278–279 K (m.p. 359.5 K).

Crystal data

$C_{21}H_{21}N$
$M_r = 287.39$
Orthorhombic, *Pbcn*
$a = 16.0767$ (12) Å
$b = 11.2793$ (10) Å
$c = 8.9528$ (5) Å
$V = 1623.4$ (2) Å^3
$Z = 4$
$D_x = 1.176$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 10 862 reflections
$\theta = 1.7$–$27.5°$
$\mu = 0.07$ mm^{-1}
$T = 150$ (2) K
Cuboid, colourless
0.63 × 0.25 × 0.17 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.609$, $T_{max} = 0.990$
16 719 measured reflections

1435 independent reflections
922 reflections with $I > 2\sigma[I]$
$R_{int} = 0.132$
$\theta_{max} = 25.0°$
$h = -19 \rightarrow 19$
$k = -13 \rightarrow 13$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.170$
$S = 1.06$
1435 reflections
103 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0936P)^2 + 0.0289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.008 (3)

H atoms were positioned geometrically and constrained as riding atoms, with a C—H distance of 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, and a C—H distance of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. The methyl H atoms on C15, which lies on a twofold axis, are disordered with equal occupancy.

Data collection: *COLLECT* (Nonius, 1998); 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*.

The authors thank the University of Western Ontario, the Xerox Research Centre (XRCC) in Mississauga, and the Natural Sciences and Engineering Council of Canada (NSERC) for their financial support of this project. We also extend our sincere thanks to Material and Manufacturing Ontario, ORDCF and CFI/OIT for their support.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brantly, T. B., Contois, L. E. & Fox, C. J. (1971). US Patent 3 567 450.
Brantly, T. B., Contois, L. E. & Fox, C. J. (1972). US Patent 3 658 520.
Chan, H. S. O., Ng, S. C., Leong, L. S. & Tan, K. L. (1995). *Synth. Met.* **68**, 199–205.
Goodbrand, H. B. & Nan-Xing, H. (1999). *J. Org. Chem.* **64**, 670–674.
Hong, Y., Senanayake, C. H., Xiang, T., Vandenbossche, C. P., Tanoury, G. J., Bakale, R. P. & Wald, S. A. (1998). *Tetrahedron Lett.* **39**, 3121–3124.

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Klupfel, K.-W., Sus, O., Behmenburg, H. & Neugebauer, W. (1965). US Patent 3 180 730.

Manifar, T., Bender, T., Goodbrand, H. B., Rohani, S., Saban, M. & Gaynor, R. (2005). *Ind. Eng. Chem. Res.* **44**, 789–798.

Manifar, T. & Rohani, S. (2004). *Can. J. Chem. Eng.* **82**, 323–334.

Manifar, T., Rohani, S. & Jennings, M. (2004). *Acta Cryst.* E**60**, o2301–o2303.

Manifar, T., Rohani, S. & Jennings, M. (2005). *Acta Cryst.* E**61**, o1032–o1034.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307-326. New York: Academic Press.

Reynolds, S. L. & Scaringe, R. P. (1982). *Cryst. Struct. Commun.* **11**, 1129–1134.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.14 for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.

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