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4-(*N*,*N*-Di-*p*-tolylamino)benzaldehyde *N*′,*N*′-diphenylhydrazone

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Key indicators

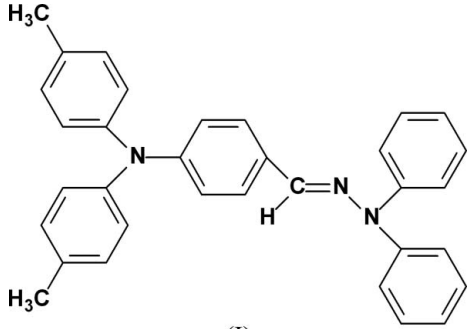
Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.126
Data-to-parameter ratio = 16.5

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

The title compound, $(p\text{-MeC}_6\text{H}_4)_2\text{NC}_6\text{H}_4\text{CH}{=}\text{NNPh}_2$ or $C_{33}H_{29}N_3$, was synthesized by the reaction of 4-(di-*p*-tolylamino)benzaldehyde and 1,1-diphenylhydrazine. The molecule is the *trans* isomer with respect to the hydrazone double bond. The central $\text{NC}_6\text{H}_4\text{CH}{=}\text{N}-\text{N}$ fragment is planar within 0.11 Å. The planes of the *p*-tolyl rings and one of the hydrazone phenyl rings form substantial dihedral angles (>60°) with the central plane of the molecule, whereas the second hydrazone phenyl ring is much closer to the central plane, the dihedral angle being 21.7 (3)°.

Comment

Hole-transporting materials (HTMs) play an important role in the manufacture of organic photoconductors (He *et al.*, 2005) and organic light-emitting diodes (Li *et al.*, 2005; Satoh *et al.*, 2003). It has been shown (Murayama, 1999) that aromatic hydrazones, usually readily available *via* the reaction of a substituted aromatic aldehyde with 1,1-diphenylhydrazine, may, in many cases, be used as high-quality HTMs.



(I)

In this paper, the structure of the title compound, (I), which exhibits HTM properties, is reported. The compound was synthesized by the reaction of 4-(di-*p*-tolylamino)-benzaldehyde and 1,1-diphenylhydrazine, obtained by reduction of *N*,*N*-diphenylnitrous amide.

The title compound, (I) (Fig. 1), is the *trans* isomer with respect to the hydrazone double bond C21=N2. Atoms N1, C15–C21, N2 and N3 of the central fragment of the molecule are coplanar within 0.11 Å. The planes of the *p*-tolyl rings (C1–C6 and C8–C13) and one of the hydrazone phenyl rings (C22–C27) form substantial dihedral angles with the central plane of the molecule [75.6 (2), 66.4 (4) and 78.2 (3)°, respectively], whereas the second hydrazone phenyl ring (C28–C33) remains much closer to the central plane [dihedral angle = 21.7 (3)°]. This conformational peculiarity is the result of steric constraints for the *ortho*-H atoms which limit the

range of energetically acceptable conformations of phenyl rings C1–C6, C8–C13 and C22–C27.

Experimental

N,*N*-Diphenylnitrous amide (6.0 g, 0.03 mol) and Zn (6.5 g, 0.10 mol) were mixed in ethanol (30 ml); thereafter acetic acid (9.3 ml, 0.16 mol) was added dropwise at 293 K. The reaction mixture was stirred for 3 h, while cooling with ice to keep the temperature below 298 K. The reaction mixture was then filtered and the filtrate, which contained 1,1-diphenylhydrazine, was refluxed for 4 h with 4-(di-*p*-tolylamino)benzaldehyde (7.6 g, 0.025 mol). The reaction mixture was cooled to room temperature and filtered. The crude product was recrystallized from ethyl acetate and the title compound was isolated in the form of yellow crystals (yield: 94.1%, m.p. 437 K).

Crystal data

$C_{33}H_{29}N_3$
M_r = 467.59
Monoclinic, $P2_1/n$
a = 12.875 (3) Å
b = 15.037 (3) Å
c = 13.591 (3) Å
β = 95.107 (4)°
V = 2620.6 (10) Å^3
Z = 4
D_x = 1.185 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2276 reflections
θ = 2.3–22.8°
μ = 0.07 mm^{-1}
T = 294 (2) K
Block, yellow
0.22 × 0.20 × 0.16 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.985, T_{max} = 0.989
14697 measured reflections
5382 independent reflections
2534 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 26.5°
$h = -14 \rightarrow 16$
$k = -18 \rightarrow 10$
$l = -17 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.126
S = 1.02
5382 reflections
327 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.0947P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

The H atoms were positioned geometrically and refined in the riding-model approximation [C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) (for methyl H atoms)].

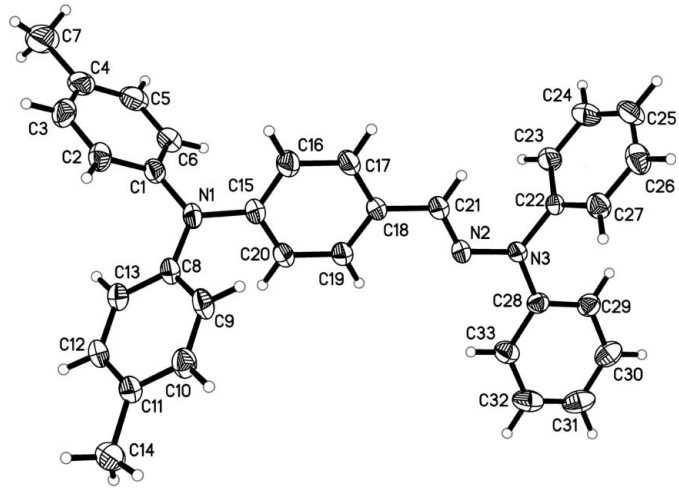


Figure 1
The molecular structure of (I), showing the atom labelling, with displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small circles of arbitrary radii.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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