

4-(*N,N*-Di-4-tolylamino)benzaldehyde (3-pyridyl-carbonyl)hydrazone monohydrate

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The crystal structure of the title compound, $C_{27}H_{24}N_4O \cdot H_2O$, containing triarylamine and benzoic hydrazone units and water of crystallization, shows a variety of hydrogen bonds, as well as features in which the N atom in the triarylamine moiety is sp^2 -hybridized and the three benzene rings are twisted with respect to one another.

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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(C-C) = 0.003\text{ \AA}$ R factor = 0.050 wR factor = 0.138

Data-to-parameter ratio = 16.1

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

Comment

The design and fabrication of efficient light-emitting devices based on organic materials has been an active research area due to their possible application in display technology (Sheets *et al.*, 1996; Dodapalapur, 1997; Mitschke & Bauerle, 2000; Tang & Anslyke, 1987; Burroughes *et al.*, 1990). One of the most fascinating advantages in using these organic materials is a wide selection of emission colors in electroluminescence displays attainable through the molecular design of organic materials (Che *et al.*, 1997). Organic materials containing the triarylamine moiety are of considerable interest for their technological applications as photoconductors and hole-transport layers (Thelakkat *et al.*, 1999; Law, 1993; Tanaka *et al.*, 1996). Compounds based on hydrazones have also played an important role in charge transport (Zhou, 1993). In this paper, the synthesis of a new compound, (I), containing triarylamine and benzoic hydrazone units, and its crystal structure are described.

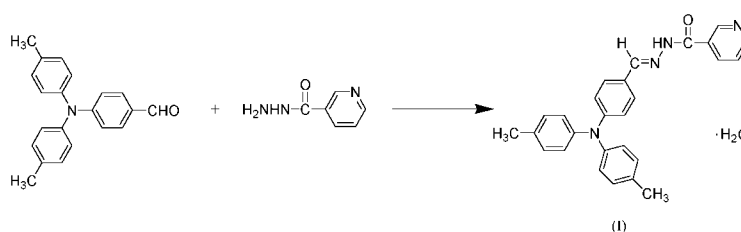


Fig. 1 is a perspective view of (I) showing the atomic numbering scheme. In the triarylamine moiety, the dihedral angle formed by the planes of C8–C13 and C14–C19 is $96.5(3)^\circ$, by C14–C19 and C21–C26 is $90.0(2)^\circ$, and by C21–C26 and C8–C13 is $48.3(3)^\circ$. Atom N4 is sp^2 -hybridized, the sum of the angles about it being 359.99° and its deviation from the plane C11/C14/C21 being only $0.0013(2)\text{ \AA}$. The dihedral angle between planes N1/C1–C5 and C8–C13 is $55.4(2)^\circ$. The torsion angles C6–N2–N3–C7 and N2–N3–C7–C8 are $169.97(18)^\circ$ and $-178.03(16)^\circ$, respectively.

In the crystalline state, compound (I) is solvated with one water molecule forming a variety of hydrogen bonds, as listed in Table 2. The crystal structure is further stabilized by weak

C7—H7···O1ⁱⁱⁱ interactions [H7···O1 = 2.54, C7···O1ⁱⁱⁱ = 3.425 (4) Å and C7—H7···O1ⁱⁱⁱ 159°; symmetry code: (iii) 1 - x, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z] between two molecules of the title compound.

Experimental

The intermediates were synthesized according to literature methods (Hallas, 1965; Yu *et al.*, 2002). A solution of 4-*N,N*-bis(4-methylphenyl)aminobenzaldehyde (0.273 g, 1 mmol) and 3-acylhydrazine pyridine (0.137 g, 1 mmol) in ethanol (20 ml) was refluxed for 5 h. The mixture was then concentrated and cooled. The reaction product was removed by filtration, washed with ethanol and purified by column chromatography on silica gel using hexane–ethyl acetate (2:1, *v/v*) as the eluant, yielding a green–yellow solid product, (I) (0.341 g, yield 87%; m.p. 496.15–497.15 K). Green–yellow single crystals suitable for X-ray analysis were obtained from an ethanol solution by slow evaporation at room temperature.

Crystal data

| | |
|---|---|
| C ₂₇ H ₂₄ N ₄ O·H ₂ O | $D_x = 1.237 \text{ Mg m}^{-3}$ |
| $M_r = 438.52$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 998 reflections |
| $a = 11.425$ (3) Å | $\theta = 2.5$ – 24.0° |
| $b = 12.404$ (4) Å | $\mu = 0.08 \text{ mm}^{-1}$ |
| $c = 17.374$ (5) Å | $T = 293$ (2) K |
| $\beta = 106.951$ (5)° | Prism, green–yellow |
| $V = 2355.3$ (12) Å ³ | $0.42 \times 0.22 \times 0.20 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|---|--|
| Bruker SMART CCD area-detector diffractometer | 4823 independent reflections |
| φ and ω scans | 3093 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $R_{\text{int}} = 0.037$ |
| $T_{\text{min}} = 0.978$, $T_{\text{max}} = 0.984$ | $\theta_{\text{max}} = 26.4^\circ$ |
| 13225 measured reflections | $h = -14 \rightarrow 9$ |
| | $k = -15 \rightarrow 15$ |
| | $l = -21 \rightarrow 21$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.4561P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.050$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.138$ | $(\Delta/\sigma)_{\text{max}} = 0.002$ |
| $S = 1.01$ | $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$ |
| 4823 reflections | $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$ |
| 300 parameters | |
| H-atom parameters constrained | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|-------------|--------------|
| N1—C1 | 1.323 (3) | N4—C11 | 1.400 (2) |
| N1—C5 | 1.337 (4) | N4—C21 | 1.422 (2) |
| N2—C6 | 1.343 (2) | N4—C14 | 1.441 (2) |
| N2—N3 | 1.386 (2) | O1—C6 | 1.229 (2) |
| N3—C7 | 1.278 (2) | C7—C8 | 1.451 (3) |
| C6—N2—N3 | 119.07 (16) | O1—C6—N2 | 123.94 (18) |
| C7—N3—N2 | 115.21 (16) | O1—C6—C2 | 120.85 (18) |
| C11—N4—C21 | 124.90 (15) | N2—C6—C2 | 115.21 (17) |
| C11—N4—C14 | 118.64 (15) | N3—C7—C8 | 121.76 (18) |
| C21—N4—C14 | 116.45 (15) | C6—N2—N3—C7 | 169.97 (18) |
| C6—N2—N3—C7 | 169.97 (18) | N3—N2—C6—C2 | 179.14 (15) |
| N3—N2—C6—O1 | -1.6 (3) | N2—N3—C7—C8 | -178.03 (16) |

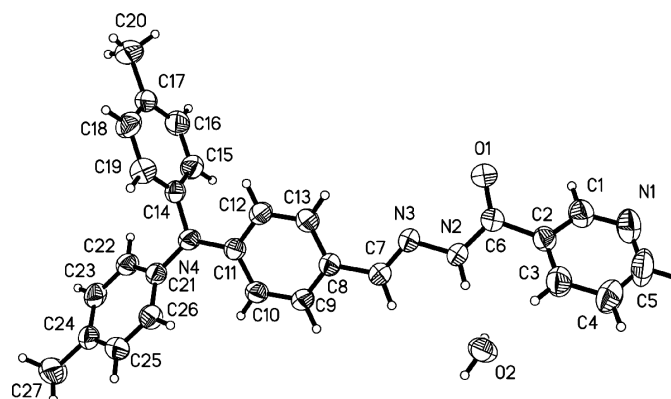


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|-------|-------------|-------------|---------------|
| N2—H2···O2 | 0.86 | 1.99 | 2.810 (2) | 160 |
| O2—H2A···N1 ⁱ | 0.86 | 2.23 | 2.853 (3) | 129 |
| O2—H2B···O1 ⁱⁱ | 0.85 | 2.12 | 2.845 (2) | 142 |
| O2—H2B···N3 ⁱⁱ | 0.85 | 2.54 | 3.282 (2) | 147 |

Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) 1 - x, y - $\frac{1}{2}$, $\frac{1}{2}$ - z.

Water H atoms were placed geometrically and were made to ride on the parent atom O2 (O—H = 0.85 Å). Other H atoms were positioned geometrically (0.86 Å for N—H, 0.93 Å for C—H and 0.96 Å for methyl C—H) and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$ for methyl H atoms and $1.2U_{\text{eq}}$ for all other H atoms.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1998); molecular graphics: SHELXTL (Sheldrick, 1998); software used to prepare material for publication: SHELXL97.

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