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The crystal structure of tris(2-bromo-4-methylphenyl)amine, $C_{21}H_{18}Br_3N$

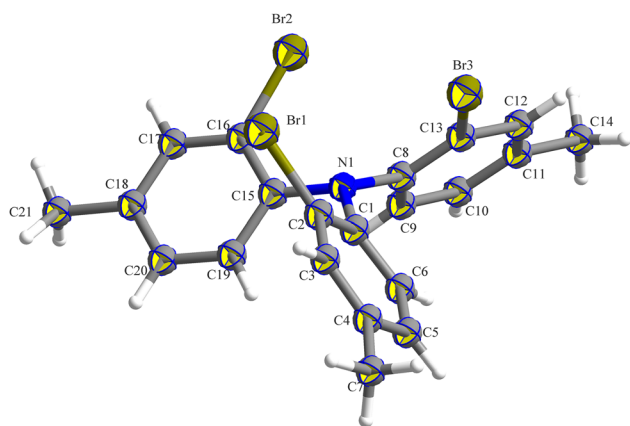


Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.14 × 0.12 × 0.10 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	7.46 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy R, ω
$\theta_{\max}$, completeness:	73.5°, 96 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12,515, 3,884, 0.058
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3,358
$N(\text{param})_{\text{refined}}$:	229
Programs:	Olex2, ¹ SHELX ^{2,3}

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Abstract

$C_{21}H_{18}Br_3N$, monoclinic, $P2_1/c$ (no. 14), $a = 17.0082(5)$ Å, $b = 7.70818(16)$ Å, $c = 15.8792(5)$ Å, $\beta = 105.108(3)^\circ$, $V = 2009.83(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0594$, $wR_{\text{ref}}(F^2) = 0.1687$, $T = 100$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

All chemicals were purchased from commercial sources and used as received. Procedures for the synthesis of tris(2-bromo-4-methylphenyl)amine was adapted from the reported paper.⁴ In a 250 mL round-bottom flask, 2.72 g (7.15 mmol) of tris(p-tolyl)amine, 3.82 g (21.5 mmol) of *N*-bromosuccinimide (NBS), 0.519 g (2.14 mmol) of benzoyl

peroxide, and 100 mL of carbon tetrachloride were combined. The mixture was refluxed at 70 °C for 6 h. Once the reaction was finished by TLC analysis, the solid residue was removed through vacuum filtration, and the filtrate was evaporated to yield crude products. The resulting white products were then purified using column chromatography on silica gel, with petroleum ether (PE) as the eluent, resulting in a white product weighing 2 g, which corresponds to a yield of 78 %. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.40 (d, $J = 2.0$ Hz, 3H), 6.99 (dd, $J = 8.3$, 1.9 Hz, 3H), 6.69 (d, $J = 8.1$ Hz, 3H), 2.30 (s, 9H). Single crystals of the desired product were obtained using the solvent thermal method over a period of two days at 85 °C, with a solvent mixture of ethanol and water in a 4:1 ratio.

2 Experimental details

Single-crystal X-ray diffraction data for the title structure was collected on XtaLAB Synergy R, DW system, HyPix diffractometer using Olex2,¹ the structure was solved with ShelXS² structure solution program using Direct Methods and refined with the ShelXL³ refinement package. The positions of the hydrogen atoms were generated geometrically. The cif-file of the title compound can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif (2379568).

3 Comment

The photophysical characteristics of highly reactive free radicals across different states have garnered significant

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} ^a /U _{eq}
Br1	0.69537 (4)	1.10083 (7)	0.28340 (5)	0.0395 (2)
Br2	0.90315 (5)	0.86413 (10)	0.46962 (5)	0.0450 (2)
Br3	0.64850 (4)	0.79336 (8)	0.47175 (4)	0.0385 (2)
C1	0.6688 (3)	0.7351 (7)	0.2742 (4)	0.0249 (11)
C2	0.6376 (4)	0.8954 (7)	0.2401 (4)	0.0304 (12)
C3	0.5653 (4)	0.9062 (8)	0.1761 (4)	0.0338 (13)
H3	0.5458	1.0167	0.1533	0.041*
C4	0.5206 (4)	0.7604 (9)	0.1446 (4)	0.0372 (14)
C5	0.5489 (3)	0.6005 (8)	0.1823 (4)	0.0328 (13)
H5	0.5176	0.4987	0.1642	0.039*
C6	0.6223 (3)	0.5891 (7)	0.2456 (4)	0.0294 (12)
H6	0.6409	0.4792	0.2699	0.035*
C7	0.4441 (4)	0.7709 (11)	0.0701 (5)	0.0506 (18)
H7A	0.3963	0.7537	0.0927	0.076*
H7B	0.4456	0.6806	0.0271	0.076*
H7C	0.4410	0.8852	0.0424	0.076*
C8	0.7588 (3)	0.5947 (7)	0.4004 (4)	0.0268 (11)
C9	0.8117 (3)	0.4553 (8)	0.4029 (4)	0.0320 (12)
H9	0.8394	0.4440	0.3585	0.038*
C10	0.8245 (4)	0.3330 (8)	0.4692 (5)	0.0369 (14)
H10	0.8620	0.2412	0.4702	0.044*
C11	0.7836 (4)	0.3424 (8)	0.5339 (4)	0.0332 (13)
C12	0.7299 (3)	0.4796 (7)	0.5324 (4)	0.0297 (12)
H12	0.7010	0.4879	0.5759	0.036*
C13	0.7187 (3)	0.6045 (7)	0.4669 (4)	0.0258 (11)
C14	0.7968 (5)	0.2083 (9)	0.6058 (5)	0.0467 (17)
H14A	0.8387	0.2496	0.6567	0.070*
H14B	0.8146	0.0990	0.5852	0.070*
H14C	0.7457	0.1895	0.6222	0.070*
C15	0.8144 (3)	0.7616 (7)	0.2990 (4)	0.0262 (11)
C16	0.8882 (4)	0.8283 (7)	0.3497 (4)	0.0282 (11)
C17	0.9513 (4)	0.8702 (8)	0.3144 (4)	0.0337 (13)
H17	1.0006	0.9141	0.3511	0.040*
C18	0.9444 (4)	0.8495 (8)	0.2261 (5)	0.0348 (13)
C19	0.8079 (3)	0.7418 (8)	0.2106 (4)	0.0293 (12)
H19	0.7589	0.6968	0.1737	0.035*
C20	0.8713 (4)	0.7861 (8)	0.1748 (4)	0.0330 (13)
H20	0.8645	0.7727	0.1138	0.040*
C21	1.0145 (4)	0.8933 (9)	0.1870 (5)	0.0434 (16)
H21A	1.0513	0.9751	0.2252	0.065*
H21B	0.9931	0.9460	0.1294	0.065*
H21C	1.0442	0.7870	0.1811	0.065*
N1	0.7477 (3)	0.7236 (6)	0.3347 (3)	0.0254 (9)

attention in the research community.^{5–7} Triaromatic amine derivatives are acknowledged for their exceptional electroactive and photoactive properties, enabling them to effectively generate free radicals *via* electrochemical processes or ultraviolet irradiation. Consequently, these materials are extensively employed in optoelectronic applications.^{8,9}

This study reports the synthesis of brominated trianiline crystals, which hold considerable promise for the advancement of optical and sensor devices.

The asymmetric unit contains one molecule of tris(2-bromo-4-methylphenyl)amine (see the figure). The bond lengths and angles within the molecule fall within the expected ranges.¹⁰ The steric hindrance caused by the bromine atom prevents the nitrogen atom at the center of the molecule from achieving a coplanar arrangement with the adjacent carbon atoms. The bond angles involving nitrogen and the connected carbon atoms C1–N1–C18, C1–N1–C8, and C8–N1–C18 measure 115.06°, 117.26°, and 118.03°, respectively. Consequently, the nitrogen and the benzene ring ultimately form a spiral, fan-like configuration. The distances of Br1–C2, Br3–C13, Br2–C16, N2–C1, N1–C15, and N1–C18 are 1.896(6) Å, 1.897(6) Å, 1.435(7) Å, 1.425(7) Å, and 1.418(7) Å.

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Conflict of interest: The authors declare no conflicts of interest regarding this article.

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