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Crystal structure of bis-(5-bromo-2-methyl-phenyl)-diazene, $C_{14}H_{12}Br_2N_2$

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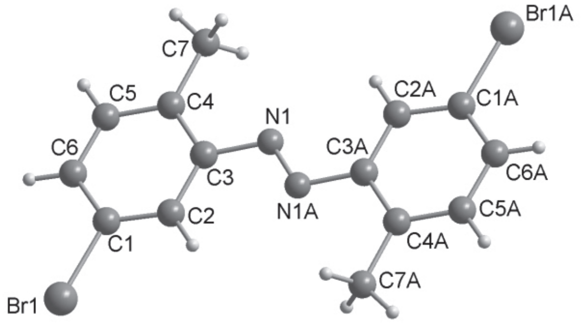

Abstract

$C_{14}H_{12}Br_2N_2$, monoclinic, $P2_1/c$ (no. 14), $a = 7.07(1)$ Å, $b = 4.079(7)$ Å, $c = 23.86(4)$ Å, $\beta = 90.13(2)°$, $V = 687.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0346$, $wR_{ref}(F^2) = 0.1166$, $T = 296$ K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.11×0.20×0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	58.77 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4689, 1262
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1010
$N(param)_{refined}$:	83
Programs:	SHELX [11]

Source of material

The oxidative homo-coupling of anilines to diphenyldiazenes was carried out under air in a 25 ml reaction tube using a Radleys Carousel Reactor™ equipped with a magnetic stirrer. 4-Methoxybenzenamine (15 mg, 4 mmol) was dissolved in 9 ml acetonitrile, CuBr (21 mg, 0.15 mmol) and TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl, 23.4 mg, 0.15 mmol) were then added. The reaction mixture was stirred vigorously at 60 °C for 18 h. After completion, the reaction mixture was extracted with diethyl ether. Then the organic layer was washed with water and brine. The organic phase was dried with anhydrous magnesium sulfate and filtered through a short silica column. After concentrating the sample under vacuum without further purification, the sample was cooled to room temperature and filtered. The obtained solid was washed by deionized water and dried. Then the yellow block-shaped crystals suitable for X-ray diffraction study were obtained.

Experimental details

Aromatic hydrogen atoms were assigned with $U_{iso}(H) = 1.2\ U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with $d(C–H) = 0.93$ Å, the methyl hydrogen atoms were assigned with $U_{iso}(H) = 1.5U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with $d(C–H) = 0.96$ Å.

Discussion

Due to the potentially interesting properties and flexibility in aspects such as composition and topology of coordination polymers (CPs), the crystal engineering of CPs is an exciting area of supramolecular chemistry [1–3]. For the high coordination numbers, along with special magnetic elements for constructing CPs has attracted a lot of interest [4]. Designing solids with molecules that encode well defined non-covalent interactions has recently become a rapidly growing area of research due to their fascinating molecular and supramolecular structural diversity and potential applications for catalysis [5] and material sciences [6–9]. Substituted aromatic azo compounds are also important units in the area of nonlinear optics, optical storage media, chemo sensors, photochemical switches and electronic devices. For these reasons, the efficient synthesis of benzene derivatives continues to attract the interest of synthetic chemists. In this contribution, we report on the interesting new compound. The title structure comprises a 5-bromo-2-methyl-phenylamine in the asymmetric unit. The whole molecule is almost planar with the maximum deviation of 0.0032 Å for N1. In addition, the bond length of N1–C3 is found to be only 1.424(5) Å. The bond C1–Br1 and C4–C7 are single bonds, confirmed by the bond lengths of 1.906(4) Å and 1.517(6) Å, respectively. Further consolidating the stability of the chain structure. Individual chains are entirely cohered together by the weak effect of van der Waals force into a 3D supramolecular network.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.2731	0.5449	0.4195	0.046
H(5)	4*e*	0.7431	–0.0531	0.3312	0.054
H(6)	4*e*	0.4768	0.0988	0.2821	0.054
H(7A)	4*e*	0.9375	–0.0623	0.4117	0.078
H(7B)	4*e*	0.8210	–0.0859	0.4674	0.078
H(7C)	4*e*	0.9181	0.2454	0.4506	0.078

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*e*	0.5639(5)	0.4180(9)	0.4890(1)	0.038(2)	0.054(2)	0.034(2)	–0.001(2)	–0.006(1)	0.001(2)
C(1)	4*e*	0.3501(5)	0.335(1)	0.3468(2)	0.039(2)	0.042(2)	0.036(2)	–0.006(2)	–0.009(2)	0.003(2)
C(2)	4*e*	0.3680(5)	0.425(1)	0.4020(2)	0.034(2)	0.046(2)	0.036(2)	0.000(2)	–0.003(2)	0.002(2)
C(3)	4*e*	0.5322(5)	0.333(1)	0.4318(1)	0.037(2)	0.043(2)	0.031(2)	–0.002(2)	–0.002(2)	0.005(2)
C(4)	4*e*	0.6773(5)	0.156(1)	0.4053(2)	0.033(2)	0.041(2)	0.045(2)	–0.001(2)	–0.002(2)	0.004(2)
C(5)	4*e*	0.6500(6)	0.069(1)	0.3492(2)	0.045(2)	0.048(2)	0.043(2)	0.004(2)	0.004(2)	–0.003(2)
C(6)	4*e*	0.4904(6)	0.157(1)	0.3196(2)	0.055(3)	0.044(2)	0.035(2)	–0.005(2)	0.000(2)	–0.002(2)
C(7)	4*e*	0.8547(6)	0.054(1)	0.4366(2)	0.037(2)	0.059(3)	0.060(3)	0.011(2)	–0.008(2)	0.005(2)
Br(1)	4*e*	0.13112(6)	0.4638(1)	0.30550(2)	0.0507(4)	0.0652(4)	0.0461(3)	0.0031(2)	–0.0198(2)	0.0002(2)

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