



NOTE

Solvent Evaporation Method and Crystal Structure of *bis*-(5-Bromo-2-methyl-phenyl)diazene

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One new diazene compound from 4-methoxybenzenamine, CuBr and 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) has been successfully synthesized. Compound shows a one-dimensional framework. The 3D supramolecular structure is formed *via* hydrogen bonding connection.

Keywords: Solvent evaporation, Crystal structure, Diazene.

Due to the interesting properties and flexibility in aspects such as composition and topology of coordination polymers, the crystal engineering of coordination polymers is an exciting area of supramolecular chemistry¹. For the high coordination numbers, along with special magnetic elements for constructing coordination polymers has attracted a lot of interest². Designing solids with molecules that encode well defined noncovalent interactions has recently become a rapidly growing area of research due to their fascinating molecular and supramolecular structural diversity and potential applications for catalysis³ and material sciences⁴. Substituted aromatic azo compounds are also important units in the area of nonlinear optics, optical storage media, chemo sensors, photochemical switches and electronic devices. Therefore, characterization of aromatic azo compounds has attracted great attention. For these reasons, the efficient synthesis of benzene derivatives continues to attract the interest of synthetic chemists. In this context, we report the synthesis of the *bis*-(5-bromo-2-methyl-phenyl)diazene.

All reagent and solvents employed were commercially available and used as received without further purification.

A mixture of 4-methoxybenzenamine (15 mg, 4 mmol) was dissolved in 9 mL acetonitrile, CuBr (21 mg, 0.15 mmol) and 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (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. Yellow crystals of the compound formed (Fig. 1).

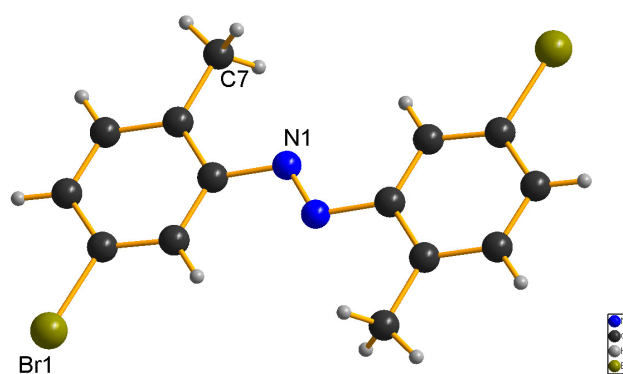


Fig. 1. Molecular structure of the title compound at 30 % probability displacement ellipsoids

Detection method: Diffraction intensity data of the single crystal of the compound was collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) by using a ω -scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallo-

graphic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT SUMMARY FOR C_7H_6BrN

Empirical formula	C_7H_6BrN
Formula weight	184.04
Crystal system space group	Monoclinic, $P2(1)/c$
Unit cell dimensions	$a = 7.065(12) \text{ \AA}$; $b = 4.079(7) \text{ \AA}$; $c = 23.86(4) \text{ \AA}$
Volume (\AA^3)	688(2)
θ range for data collection	2.88-25.49
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0346$; $wR_2 = 0.1012$
Z, Calculated density (mg/m^3)	4, 1.778
Absorption coefficient (mm^{-1})	5.877
F(000)	360
Limiting indices	$-8 \leq h \leq 8$; $-4 \leq k \leq 4$; $-28 \leq l \leq 28$
Largest diff. peak and hole ($e/\text{\AA}^3$)	0.452 and -0.305
Goodness-of-fit on F^2	0.807
R indices (all data)	$R_1 = 0.0468$; $wR_2 = 0.1166$

TABLE-2
SELECTED BOND LENGTHS (\AA)
AND ANGLES ($^\circ$) FOR C_7H_6BrN

N(1)-C(3)	1.424(5)	C(1)-Br(1)	1.906(4)
N(1)#1-N(1)-C(3)	115.1(4)	C(2)-C(1)-Br(1)	119.7(3)
C(6)-C(1)-Br(1)	118.7(3)	C(4)-C(3)-N(1)	116.4(3)
C(2)-C(3)-N(1)	123.0(3)	C(5)-C(4)-C(3)	117.6(4)

X-ray diffraction reveals that the symmetric unit is composed of 5-bromo-2-methyl-phenylamine molecule. In the phenylamine are fragment, the benzene ring is almost planar with the maximum deviation of $0.0032(37) \text{ \AA}$ for N(1). In addition, in the molecules of the title compound, the bond

length of N(1)-N(1)#1, N(1)-C(3) are found to be only $1.241(7) \text{ \AA}$, $1.424(5) \text{ \AA}$, respectively. The bond C(1)-Br(1) and C(4)-C(7) is a single bond, which can rotate and this is confirmed by the bond length of $1.906(4) \text{ \AA}$, $1.517(6) \text{ \AA}$. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 3D framework (Fig. 2).

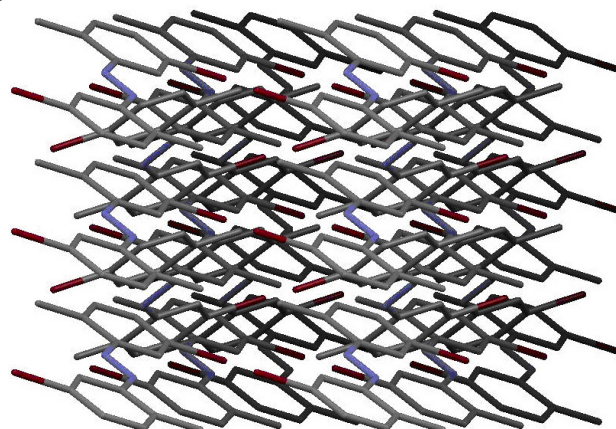


Fig. 2. 3D structure formed via hydrogen bonding interactions

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