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Solution Studies and Crystal Structure of 1,3-*bis*[2-(Trifluoromethyl)phenyl]triaz-1-ene

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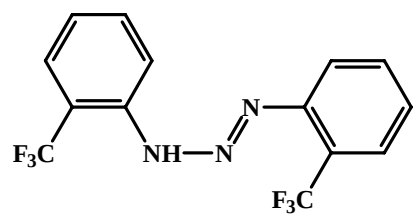
The crystal structure of 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene is monoclinic, space group cc with a = 15.154(3), b = 4.7713(10), c = 19.054(4) Å, β = 103.235(7)° and Z = 4. The crystal structure was solved by direct methods and refined by full-matrix least squares to final values of R1 = 0.0439 and wR2 = 0.1209 with 1670 reflections ($I > 2\sigma(I)$). The 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene is involved in weak C–H···F hydrogen bonding and F···F interactions. The results of studies of the stoichiometry and formation of complexes of 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene with metal ions in the acetonitrile solution were found that mole ratio is 1.

Key Words: Triazenes, X-ray structure, Single crystal, Hydrogen bond, Solution studies.

INTRODUCTION

Aryl triazenes have been studied over 130 years for their interesting structural, anticancer and reactivity properties. They have been used in medicinal, combinatorial chemistry, in natural synthesis and as organometallic ligands[1]. The first extensive investigation of the coordination chemistry of a triazene derivative (1,3-diphenyltriazene) was carried out in 1887 by Meldola and Streatfield[2].

Triazene compounds characterized by having a diazoamino group (–N=NN⟨) commonly adopt a *trans* configuration in the ground state[3]. In this paper, the synthesis and crystalline structure of a new molecule 1,3-*bis*[2-(trifluoromethyl)phenyl]-triaz-1-ene have been reported (**Scheme-I**).



Scheme-I: Chemical structure of 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene

EXPERIMENTAL

The title compound was prepared as follows: A 1 L beaker was charged with 100 g of ice and 150 mL of water and then cooled in an ice-bath. To this, 16.11 g (0.10 mol) of 2-(trifluoromethyl)aniline and 13 g (0.13 mol) of hydrochloric acid (d = 1.18 g/mL) were added. To this mixture a solution of $NaNO_2$ prepared by dissolving 4.10 g (0.06 mol) in minimum quantity of water, was added in drop-wise under constant stirring. After complete addition, the solution was stirred for another 15 min. During this time a solution of sodium acetate 14.76 g (0.18 mol) in 45 mL of water was added to maintained the pH of solution around 5. After stirring for another 35 min, the brown precipitate thus formed was filtered under suction. The yield of crude product was 55 % and recrystallized twice from ethanol to give light yellow needle shape crystals. Melting point 170 °C. Found C, 50.30; H, 2.60; N, 12.30: calculated for $C_{14}H_9N_3F_6$; C, 50.41; H, 2.70; N, 12.60 %.

The brunched tube method was employed for preparation of suitable single crystals. The title compound (0.2 g) was placed in one arm of a branched tube, acetonitrile was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 50 °C while the other was at ambient temperature. After 7 d, crystals were deposited in the cooler arm which was filtered off, washed with ether and air dried. The absorbance spectrum of the triazene solution were recorded after each addition of transition metal ion solution on a computerized double-beam Shimadzu 1634 spectrophotometer, using two matched 10 mm quartz cells.

RESULTS AND DISCUSSION

Crystallographic measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. Structure of 1,3-*bis*[2-(trifluoromethyl)phenyl]-triaz-1-ene was solved by direct methods and refined by full-matrix least squares techniques on F^2 using SHELXTL[4]. The N-H hydrogen atom was located in the difference density Fourier map and its positions was refined with an N-H distance of 0.88 Å within a standard deviation of 0.02 Å. All other hydrogen atoms were placed in calculated positions and all H atoms were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon or nitrogen atom. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

The corresponding crystal data and structure refinements are summarized in Table-1 and all atomic coordinates and equivalent isotropic displacement parameters are given in Table-2. The crystal structure is found to be monoclinic, space

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT DETAILS FOR
1,3-*BIS*[2-(TRIFLUOROMETHYL)PHENYL]TRIAZ-1-ENE

Empirical formula	$C_{14}H_9N_3F_6$
Formula weight	333.24
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, cc
Unit cell dimensions	a = 15.154(3) Å b = 4.7713(10) Å c = 19.054(4) Å
Volume	1341.1(5) $Å^3$
Z, Calculated density	1.651 Mg/m^3
Absorption coefficient (MoK_α)	0.159 mm^{-1}
F(000)	672
Crystal size	0.55 mm × 0.50 mm × 0.39 mm
θ Range for data collection	2.20 to 28.28 deg.
Limiting indices	$-20\leq h\leq 20$, $-6\leq k\leq 6$, $-25\leq l\leq 25$
Reflections collected / unique	6373/1670 [R(int) = 0.0265]
Completeness to theta = 28.28	99.9 %
Absorption correction	Multi-scan
Max. and min. transmission	0.940 and 0.724
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1670/3/211
Goodness-of-fit on F2	1.153
Final R indices [for 4055 rfls with $I > 2\sigma(I)$]	R1 = 0.0439, wR2 = 0.1209
R indices (all data)	R1 = 0.0441, wR2 = 0.1211
Largest diff. peak and hole	0.649 and -0.340 e. $Å^{-3}$
(Δ/δ)max	0.000

TABLE-2
ATOMIC COORDINATES [× 10^4] AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS [$Å^2 \times 10^3$] FOR 1,3-*BIS*[2-(TRIFLUOROMETHYL)PHENYL]-TRIAZ-1-ENE. U(eq) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED U_{ij} TENSOR

	x	y	z	U(eq)
C(1)	779(2)	2480(5)	4346(1)	24(1)
C(2)	1795(2)	2295(5)	4613(1)	20(1)
C(3)	2276(2)	405(5)	4286(1)	24(1)
C (4)	3212(2)	187(6)	4519(2)	26(1)
C(5)	3669(2)	1877(6)	5084(2)	26(1)
C(6)	3193(2)	3758(5)	5419(1)	24(1)
C(7)	2249(2)	3973(5)	5190(1)	20(1)
C(8)	2045(2)	10858(5)	6847(1)	19(1)
C(9)	2992(2)	11180(5)	7060(1)	21(1)
C(10)	3366(2)	13082(6)	7602(2)	25(1)
C(11)	2809(2)	14694(6)	7937(1)	25(1)

	x	y	z	U(eq)
C(12)	874(2)	14371(5)	7729(1)	23(1)
C(13)	1491(2)	12452(5)	7194(1)	19(1)
C(14)	477(2)	12131(5)	6988(2)	24(1)
F(1)	474(1)	888(4)	3757(1)	33(1)
F(2)	489(1)	5111(4)	4157(1)	31(1)
F(3)	324(1)	1645(4)	4841(1)	33(1)
F(4)	64(1)	13510(4)	7438(1)	33(1)
F(5)	109(1)	13072(5)	6319(1)	37(1)
F(6)	207(1)	9426(4)	6995(1)	33(1)
N(1)	1725(1)	5801(5)	5515(1)	22(1)
N(2)	2181(1)	7396(5)	6020(1)	21(1)
N(3)	1644(1)	9003(5)	6294(1)	21(1)

group cc with a = 15.154(3), b = 4.7713(10), c = 19.054(4) Å, β = 103.235(7)° and Z = 4. The crystal structure was solved to final values R1 = 0.0439 and wR2 = 0.1209 with 1670 reflections (I > 2σ(I).

The crystal (Fig. 1) consists of a discrete molecule. The torsion angles of C(7)-N(1)-N(2)-N(3) and N(1)-N(2)-N(3)-C(8) are -179.6(2) and -179.8(2))° and the triaz-1-ene group is planar. The bond lengths and angles are within the expected ranges. As it is seen from Fig. 2, the molecule is involved in weak inter-hydrogen bonding with CH of phenyl groups acting as donors and F atoms as acceptors. There are F···F interactions between the neighboring molecules.

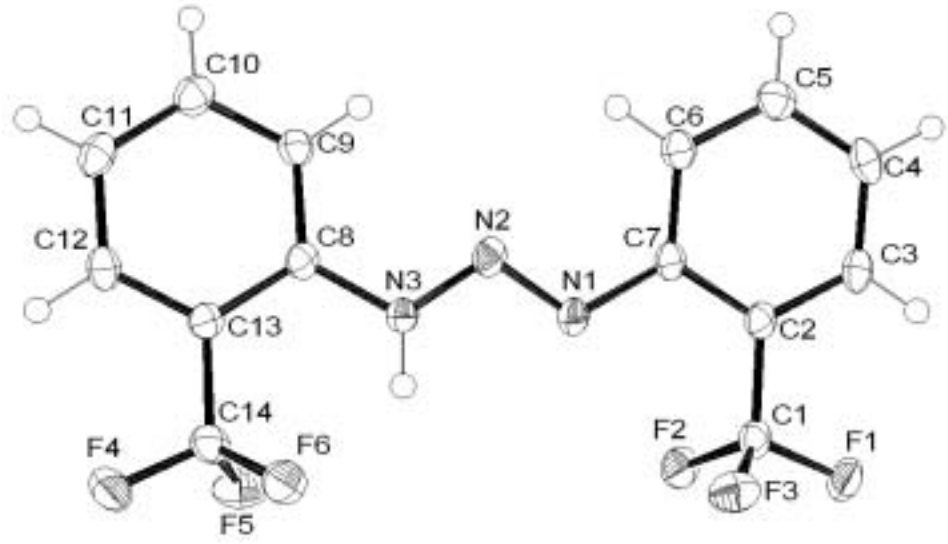


Fig. 1. ORTEP diagram showing hydrogen bonding in 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene

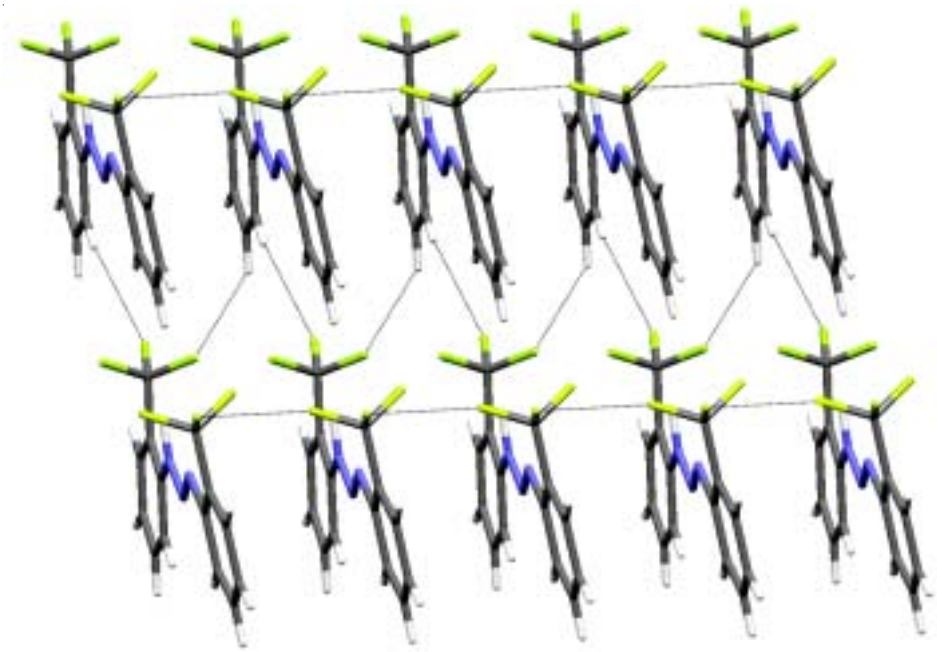


Fig. 2. Packing and showing F···F and F···H interactions between the parallel molecules in 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene crystal

The packing of the resulting crystal, shown in Fig. 2, clearly revealed that a two-dimensional network is formed owing to the presence of intermolecular weak hydrogen-bonding and F···F interactions.

The complexation of molecule 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene in the presence of increasing concentration of the different metal ions was studied spectrophotometrically in acetonitrile solution at room temperature. For the sake of simplicity, only variation absorption spectra of title compound with namely Ni^{2+} is shown. As is obvious in Fig. 3, the strong absorption of the ligand at about 330 nm increases with increasing concentration of the Ni^{2+}. In all cases studied, the resulting absorbance as a function of [metal ion]/[triazene] mole ratio plot for different metal ions shown in Fig. 4. As can be seen from Fig. 4, in all cases studied, absorbance-mole ratio plots causes no significant change in absorbance changes where metal ion-to-triazene mole ratio is 1 and further addition of the metal ion causes a rather continuous increases in the absorbance of the solution. Such an absorbance behaviour is indicative of the formation of a 1:1 complex in solution[5,6].

Supplementary material: Complete bond lengths and angles, coordinates and displacement parameters have been deposited at Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 663472 for 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene.

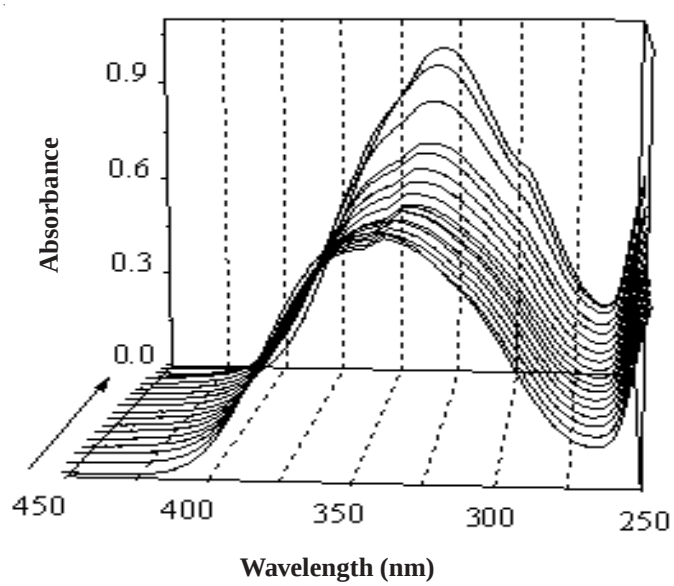


Fig. 3. Absorbance spectra of a 5×10^{-5} mol L^{-1} 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene solution in acetonitrile, at different Ni^{2+} concentrations. The arrow shows the directions of absorbance changes by increasing the metal ion concentration

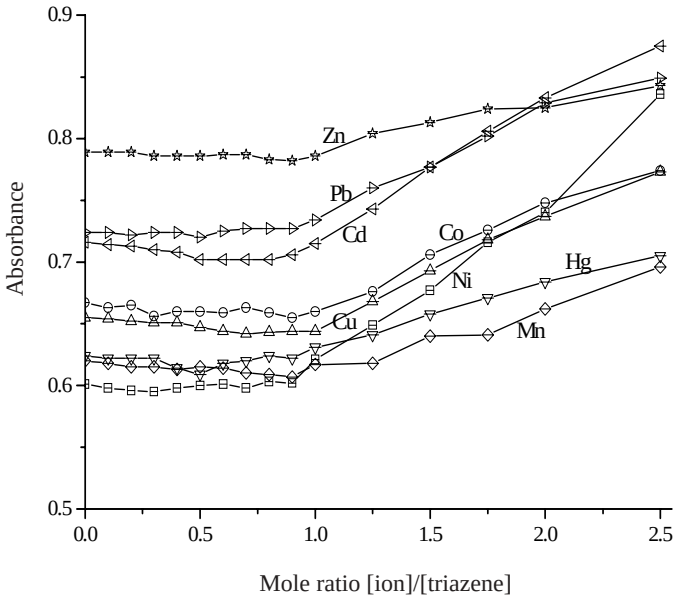


Fig. 4. Absorbance of a 5×10^{-5} mol L^{-1} 1,3-*bis*[2-(trifluoromethyl)phenyl]triaz-1-ene solution at about 330 nm, as a function of metal ion/triazene mole ratio for different metal ions

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