Synthesis and Crystal Structure of 1-*p*-Tolyl-3-(3-(trifluoromethyl)phenyl)-triaz-1-ene 1-oxide

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The crystal structure of 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide is triclinic, space group $P\bar{1}$ with $a = 6.065(2)$, $b = 8.391(2)$, $c = 13.529(3)$ Å, $\alpha = 82.047(5)$, $\beta = 84.350(5)$, $\gamma = 83.377(5)^\circ$, and $Z = 2$. The crystal structure was solved by direct methods, and refined by full-matrix least squares to final values of $R1 = 0.0579$ and $wR2 = 0.1453$ with 2000 reflections ($I > 2\sigma(I)$). There are intermolecular hydrogen bonds between the NH groups acting, as donors and O atoms as acceptors and F...F interactions.

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Aryl triazenes have been studied for over 130 years concerning 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 concerning the coordination chemistry of a triazene derivative (1,3-diphenyltriazene) was carried out in 1887 by Meldola.²

Triazene compounds, characterized by having a diazoamino group ($-N=NN<$), commonly adopt a *trans* configuration in the ground state.³ Hydroxytriazenes in the form of single crystal convert to the *N*-oxide form, and show the tautomeric form of structure. Kuroda⁴ synthesised and reported on 3-(4-carbamoylphenyl)-1-methyltriazene 1-oxide in both, *N*-oxide and hydroxyl forms, as well as the anti-tumour activity of this class of compounds. The molecule adopts the *N*-oxide rather than the *N*-hydroxyl form, in agreement with both spectroscopic and X-ray evidence. In this paper, we wish to report on the synthesis, crystalline structure and solution studies of a new molecule, 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide, **L** (Fig. 1).

An aqueous alcoholic (2:1) solution of 0.2 mole (26.47 g) of 4-nitrotoluene was reduced by ammonium chloride (16.0 g) and zinc dust (35 g) at a temperature of 60 – 65°C. The addition of zinc dust was completed in about 1 h. The obtained *p*-

Tolylhydroxylamine was coupled with a diazotized product of 0.1 mol (12.39 ml) of 3-aminobenzotrifluoride at 0 to 5°C. This resulted a yellowish-brown precipitate, which was filtered under suction and washed with ice-cold water. The crude product was recrystallized twice with ethanol, and yellow needles were obtained (the yield was about 60%). The m.p. of the compound was 152°C.

A branched tube method was employed for the preparation of suitable single crystals.⁵ The title compound (0.2 g) was placed in one arm of a Branched tube. Hexane was carefully added to fill both arms. The tube was then sealed and the ligand-

Table 1 Crystal data and structure refinement details for 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide

Chemical formula: C ₁₄ H ₁₂ F ₃ N ₃ O	
Formula weight = 295.27	
$T = 293(2)$ K	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 6.065(2)$ Å	$\alpha = 82.047(5)$
$b = 8.391(2)$ Å	$\beta = 84.350(5)$
$c = 13.529(3)$ Å	$\gamma = 83.377(5)$
$V = 675.0(3)$ Å ³	$Z = 2$
$D_x = 1.453$ g/cm ³	
Radiation: Mo K_α ($\lambda = 0.71069$ Å)	
$\mu(\text{Mo } K_\alpha) = 0.123$ mm ⁻¹	$F(0\ 0\ 0) = 304$
Crystal size = $0.27 \times 0.24 \times 0.13$ mm	
No. of reflections collected = 3055	
No. of independent reflections = 2000	
θ range for data collection: 2.46 to 27.45°	
Data/restraints/parameters = 3055/30/206	
Goodness-of-fit on $F^2 = 1.020$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0579$, $wR2 = 0.1453$	
R indices (all data): $R1 = 0.0896$, $wR2 = 0.1703$	
$(\Delta/\sigma)_{\max} = 0.001$	
$(\Delta\rho)_{\max} = 0.238$ e Å ⁻³	$(\Delta\rho)_{\min} = -0.244$ e Å ⁻³
Measurement: Nonius kappa-CCD diffractometer	
Program system: SHELXL-97	
Structure determination: SIR97	
CCDC deposition number: 721300

Fig. 1 Chemical structure of the title compound.

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Fig. 2 a) ORTEP representation and b) showing hydrogen bonding in the compound 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide.

containing arm was immersed in a bath at 50°C, while the other was kept at ambient temperature. After 5 days, crystals were deposited in the cooler arm, which was filtered off, washed with ether, and air dried.

Crystallographic measurements were made at 293(2)K using a Nonius kappa-CCD diffractometer. The structure of 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide was solved by direct methods, and refined by full-matrix least-squares techniques on F^2 using SHELXTL.⁶ The N-H hydrogen atom was located in a difference density Fourier map, and its positions were refined with an N-H distance of 0.87 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 of 1.5 (methyl) or 1.2-times (all others) that of the adjacent carbon or nitrogen atom.

The corresponding crystal data and structure refinements are summarized in Table 1.

The crystal (Fig. 2a) consists of a discrete molecule. The torsion angles of N(1)-N(2)-N(3)-C(8) and C(1)-N(1)-N(2)-N(3) are 176.9(1) and -179.4(1)°, and the triaz-1-ene group is planar. The bond lengths and angles are within the expected ranges. As can be seen from Fig. 2b, the molecule is involved in inter-hydrogen bonding with N-H acting as donors and O atoms of *N*-oxide groups as acceptors between the neighboring molecules. The corresponding distances and angles for the hydrogen bonds are given in Table 2.

The packing of the resulting crystal, shown in Fig. 3, clearly

Table 2 Hydrogen bond distances and angles (in Å and °, respectively) of 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide

	d(D-H)	d(H...A)	d(D...A)
N ₃ -H ₃O ₁	N(3)-H(N3)	H(N ₃).....O ₁	N ₃O ₁
	d= 0.873	d= 2.150	d=2.966
C ₆ -H ₆F ₃	C ₆ -H ₆	H ₆F ₃	C ₆F ₃
	d=0.930	d=2.559	d=3.254

Fig. 3 Packing and O...N and F...H interactions shown between the parallel molecules in the 1-*p*-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide crystal.

reveals that a one-dimensional network is formed owing to the presence of intermolecular weak hydrogen-bonding and F...H interactions between the parallel molecules. Also, there are face-to-face π - π stacking interactions between aromatic rings of the neighbor chains in this compound.

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