

Crystal Structure of 1,3-Bis(2-trifluoromethylphenyl)triazene

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The crystal structure of the title compound, C₁₄H₉F₆N₃, shows the expected stereochemistry *trans* about the N=N double bond in the diazoamine moiety. The interplanar angle [8.3(1)°] between the terminal phenyl rings indicates that the whole molecule is almost planar (r.m.s. deviation = 0.0929 Å). The molecule shows intramolecular N-H⋯(F1, F2) bifurcated, and non-classical C-H⋯F hydrogen bonds. The unequal distribution of the double-bond character among the N atoms of the diazoamine group indicates a delocalization of the π electrons over the N=N-N(H) moiety towards the terminal 2-trifluoromethylphenyl substituents.

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Free 1,3-disubstituted triazenes, RN=N-N(H)R (R = aryl or alkyl group), characterized by X-ray analysis, show always a *trans* stereochemistry about the N=N double bond. On the other hand, hydrogen bonds play an important role on geometrical aspects of molecules in the solid state. From this point of view, the diazoamino moiety of 1,3-disubstituted triazenes, N=N-N(H), provides intra and intermolecular interactions through hydrogen bonds with polarizable acceptor atoms included on the terminal aryl substituents. A review of the literature showed that no X-ray crystal data have been reported of free 1,3-diaryltriazenes including trifluoromethyl fragments attached to terminal aryl substituents. In this work, we report on the crystal structure of the title molecule, (I), (Fig. 1) based on a single-crystal X-ray structural analysis.

The synthesis of the title complex included reagents of reagent grade, which were used without further purification. Methanol was treated with metallic sodium and distilled over an argon atmosphere. A solution of *o*-trifluoromethylaniline (2.0 g, 12.3 mmol) and isopentyl nitrite (0.7 g, 6.0 mmol) in 40 mL anhydrous methanol was stirred 1 h at room temperature. The yellow precipitate of 1,3-bis(2-trifluoromethylphenyl)triazene was separated by filtration and dried over P₂O₅ under vacuum. The product was recrystallized from an acetone/pyridine/ethyl acetate/methanol mixture (1:1:1:1). Vitreous yellow bar-shaped crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation of the solvent mixture. Yield 90% (1.78 g, 5.6 mmol) based on *o*-trifluoromethylaniline, m.p. 175–177°C. IR (KBr pellet, cm⁻¹) 3354.8 (ν_{as} N-H) s; 1428.8 (ν_s N=N) vs; 1334.0 (ν_{as} C-F) vs; 1193.7 (ν_s N-N) vs (IR data: vs, very

strong; s, strong).

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). The crystal and experimental data are listed in Table 1. The structure was solved by direct methods using SIR2004.¹ The non-hydrogen atoms were refined anisotropically by the full-matrix least-square method

Table 1 Crystal and experimental data

Formula: C ₁₄ H ₉ F ₆ N ₃
Formula weight: 333.24
Crystal system: monoclinic
Space group: <i>Cc</i> Z = 4
<i>a</i> = 15.3122(12) Å
<i>b</i> = 4.8544(3) Å
<i>c</i> = 19.2804(15) Å
β = 104.205(2)°
<i>V</i> = 1389.32(18) Å ³
<i>D</i> _x = 1.593 g/cm ³
Absorption coefficient = 0.154 mm ⁻¹
<i>F</i> (0 0 0) = 672
Crystal dimensions (mm) = 0.17 × 0.17 × 0.50
<i>R</i> = 0.0307
<i>R</i> _w = 0.0833
θ range for data collection: 3.06 to 25.50°
Completeness to θ = 25.50 99.8%
Max. and min. transmission: 0.9743 and 0.9270
Goodness-of-fit = 1.075
Absolute structure Flack parameter: -0.2(6)
(Δρ) _{max} = 0.123 e.Å ⁻³
(Δρ) _{min} = -0.149 e.Å ⁻³
No. of reflections used = 2577
No. of parameters = 208
Data collection: COSMO/APEX2; Bruker, 2004 ⁷
Cell refinement and data reduction: SAINTE; Bruker, 2004 ⁷
Absorption correction: multi-scan (SADABS; Bruker, 2004) ⁷
Molecular graphics: DIAMOND ⁸

CCDC 608115 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

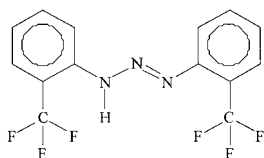


Fig. 1 Structural chemical diagram of (I).

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Table 2 Selected bond lengths (Å) and angles (°)

C1–C12	1.492(3)
C2–C22	1.490(3)
C1–F11	1.327(2)
C1–F12	1.333(2)
C1–F13	1.327(2)
C2–F21	1.337(3)
C2–F22	1.332(3)
C2–F23	1.327(2)
N11–C11	1.417(2)
N13–C21	1.398(2)
N11–N12	1.281(2)
N12–N13	1.302(2)
F11–C1–F13	106.50(18)
F11–C1–F12	105.44(18)
F13–C1–F12	105.75(17)
F23–C2–F22	106.73(17)
F23–C2–F21	105.0(2)
F22–C2–F21	105.29(17)
N12–N11–C11	115.81(14)
N12–N13–C21	118.13(14)
N11–N12–N13	111.89(14)

using SHELXL97.² The positional parameters of the H atoms bonded to C and N atoms were obtained geometrically, with the C–H and N–H distances fixed (0.93 Å for Csp²; 0.86 Å for Nsp²), and refined as riding on their respective C and N atoms, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{Csp}^2, \text{Nsp}^2)$. Attempts to locate H1 from a difference map and refinement with an isotropic displacement parameter resulted in an inconsistent value of $U_{\text{eq}} = 125(13)$. Selected bond distances and angles are given in Table 2. The molecular structure is shown in Fig. 2.

The molecular structure of (I) confirms the expected *trans* stereochemistry about the N11=N12 double bond. A typical feature of free 1,3-diaryltriazenes is delocalization of the π electrons on the triazene group towards to the terminal aryl substituents. This behavior is supported by the deviations observed from the normal N–N and C_{aryl}–N bond lengths. The N11=N12 bond [1.281(2)Å] is longer than the characteristic value for a double bond (1.236 Å), whereas the N12–N13 bond [1.302(2)Å] is shorter than the characteristic value for a single bond (1.404 Å).³ On the other hand, the N13–C21 [1.398(2)Å] and N11–C11 [1.417(2)Å] bonds are shorter than the characteristic N–C_{aryl} single bonds (secondary amines, R₂NH, R = Csp²; 1.452 Å).⁴ These values are in good agreement with those observed in similar compounds, 2-cyano-2'-nitrodiazaminobenzene [N=N = 1.258(3)Å and N=N = 1.337(3)Å]⁵, and 1-(4-chlorophenyl)-3-(2-nitrophenyl)-1-triazene [N=N = 1.255(2)Å and N–N = 1.354(2)Å].⁶

The molecule (I) shows intramolecular hydrogen bonds with a bifurcated geometry D–H...(*A*₁, *A*₂) (D = donor atom, A = acceptor atom), N13–H1...(*F*₂₁, *F*₂₃), and non-classical C–H...F hydrogen bonds (Fig. 2, Table 3). Beside the geometrical parameters mentioned in Table 3, the angle F21...H1...F23 is 51.6°, and the elevation of H1 from the plane formed by the atoms N13, F21, F23 is 0.5866(5)Å.

Due to the non-classical C–H...F hydrogen bonds, the torsion angles F13–C1–C12–C11 = 175.80(18)° and F22–C2–C22–C21 = 171.62(16)° are close to 180°, indicating co-planarity between the F13–C1 and F22–C2 fragments that bisects the CF₃ groups, and the respective attached phenyl rings.

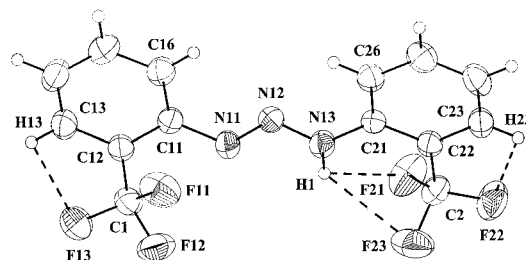


Fig. 2 Molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have arbitrary radii. The intramolecular N–H...F and C–H...F interactions are shown as dashed lines.

Table 3 Hydrogen-bonding geometric parameters (Å, °)

D–H...A	D–H	H...A	D...A	
N13–H1...F21	0.86	2.33	2.821(2)	117
N13–H1...F23	0.86	2.52	3.026(2)	119
C13–H13...F13	0.93	2.33	2.675(3)	102
C23–H23...F22	0.93	2.35	2.691(3)	101

The phenyl rings C11–C16 (r.m.s. deviation 0.0044 Å) and C21–C26 (r.m.s. deviation 0.0040 Å) are planar within the experimental error, and make an interplanar angle of 8.3(1)°, which indicates that the whole molecule is almost planar.

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