

## Crystal Structure of 1-(4-Bromophenyl)-3-(4-nitrophenyl)triazene

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The crystal structure of the title compound,  $C_{12}H_9BrN_4O_2$ , shows that the stereochemistry about the N=N double bond in the diazoamine moiety is *trans*. The dihedral angle [6.7(6)°] between the terminal phenyl rings indicates that the whole molecule is almost planar (r.m.s. deviation = 0.0945 Å). Intermolecular N-H...O and C-H...O hydrogen bonds generate infinite one-dimensional linear chains along the [0 0 1] direction. The unequal distribution of the double-bond character among the N atoms of the diazoamine moiety indicates a delocalization of the  $\pi$  electrons over the N=N-N(H) moiety towards the terminal aryl substituents.

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1,3-Disubstituted triazenes, RN=N-N(H)R (R = aryl or alkyl group), characterized by X-ray analysis show a *trans* stereochemistry about the N=N double bond. On the other hand, hydrogen bonds play an important role in the self-assembling of molecules in crystal, structures including supramolecular arrays. The diazoamino moiety of 1,3-disubstituted triazenes, N=N-N(H), provides intermolecular interactions through hydrogen bonds with polarizable acceptor atoms of the terminal aryl substituents, giving rise to supramolecular arrays. As part of a study of intermolecular interactions through hydrogen bonds in the solid state of asymmetric disubstituted 1,3-diaryltriazenes, 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 and solvents of reagent grade, which were used without further purification. *p*-Nitroaniline (0.83 g, 6.0 mmol) was added with continuous stirring to a mixture of 20 mL glacial acetic acid and 5 mL of water. The resulting solution was cooled to -3°C. A sodium nitrite solution (0.41 g, 6.0 mmol) in water (5 mL) was slowly added with continuous stirring. A solution of *p*-bromoaniline (1.03 g, 6.0 mmol) in glacial acetic acid (5 mL) was added to the reaction mixture. Stirring was continued for 20 min at a temperature of between -3 and -5°C. The resulting reaction mixture was neutralized with a 30% aqueous solution of sodium acetate. The yellow crude product, separated by filtration, was washed with small portions of cool water and dried over  $P_2O_5$  under vacuum. The product was recrystallized

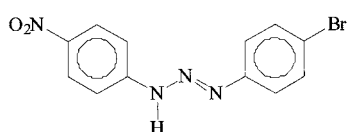


Fig. 1 Structural chemical diagram of (I).

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from an acetone/toluene mixture (2:1). Yellow bar-shaped crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation of the solvent mixture. Yield 90% (1.73 g, 5.4 mmol) based on *p*-bromoaniline, m.p. 183°C. IR (KBr pellet,  $cm^{-1}$ ) 3287.7 ( $\nu_{as}$  N-H) vs; 1511.0 ( $\nu_{as}$  NO<sub>2</sub>) vs; 1397.3 ( $\nu_s$  N=N) s; 1333.6 ( $\nu_s$  NO<sub>2</sub>) vs; 1166.8 ( $\nu_s$  N-N) vs. (IR data: vs, very strong; s, strong). Anal. Calcd for  $C_{12}H_9BrN_4O_2$ : C, 44.88; H, 2.82; N, 17.45. Found C, 45.17; H, 2.38; N, 17.31. <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm):  $\delta$  7.54 - 7.66 (m, 6H, BrC<sub>6</sub>H<sub>4</sub> and

Table 1 Crystal and experimental data

Formula:	$C_{12}H_9BrN_4O_2$
Formula weight:	321.14
Crystal system:	orthorhombic
Space group:	<i>Pbca</i> $Z = 8$
<i>a</i> =	10.833(2) Å
<i>b</i> =	17.176(2) Å
<i>c</i> =	13.818(2) Å
<i>V</i> =	2571.1(7) Å <sup>3</sup>
<i>D<sub>x</sub></i> =	1.659 g/cm <sup>3</sup>
Absorption coefficient =	3.201 mm <sup>-1</sup>
<i>F</i> (0 0 0) =	1280
Crystal dimensions (mm) =	0.40 × 0.40 × 0.13
<i>R</i> =	0.0693
<i>R<sub>w</sub></i> =	0.1473
$\theta$ range for data collection:	2.38 to 25.48°
Completeness to $\theta = 25.48$	100.0%
Goodness-of-fit =	0.961
( $\Delta\rho$ ) <sub>max</sub> =	0.634 e.Å <sup>-3</sup>
( $\Delta\rho$ ) <sub>min</sub> =	-0.777 e.Å <sup>-3</sup>
No. of reflections used =	2392
No. of parameters =	176
Data collection:	CAD-4 EXPRESS <sup>8</sup>
Cell refinement:	CAD-4 EXPRESS <sup>8</sup>
Data reduction:	XCAD4 <sup>9</sup>
Molecular graphics:	DIAMOND <sup>10</sup>
Absorption correction:	$\Psi$ scan <sup>11</sup>
CCDC	605438

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

C14-Br	1.901(8)	N12-N11-C11	112.8(7)
N1-O12	1.190(8)	N12-N13-C21	121.3(9)
N1-O11	1.194(8)	C15-C14-Br	119.6(6)
N11-N12	1.257(8)	C13-C14-Br	119.2(7)
N12-N13	1.326(10)	O12-N1-O11	125.4(8)
N13-H1	0.65(7)	N11-N12-N13	110.9(7)

H2,H2'-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>), 8.25 - 8.33 (m, 2H, H3,H3'-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>), 9.90 (s, 1H, NH); <sup>13</sup>C NMR (75.47 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ 116.1 (s, C3,C3'-BrC<sub>6</sub>H<sub>4</sub>), 121.4 (s, Br-C), 123.3 (s, C2,C2'-BrC<sub>6</sub>H<sub>4</sub>), 126.5 (s, C2,C2'-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>), 133.3 (s, C3,C3'-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>), 144.0 (s, NH-N=N-C), 148.3 (s, N=N-NH-C), 149.4 (s, O<sub>2</sub>N-C).

The X-ray data were collected by graphite-monochromated Mo K<sub>α</sub> radiation (λ = 0.71073 Å). The crystal and experimental data are listed in Table 1. The structure was solved by direct methods using SIR2004.<sup>1</sup> The non-hydrogen atoms were refined anisotropically by the full matrix least-square method using SHELXL97.<sup>2</sup> The positional parameters of the H atoms bonded to C atoms were obtained geometrically, with the C-H distances fixed (0.93 Å for Csp<sup>2</sup>), and refined as riding on their respective C atoms, with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(Csp<sup>2</sup>). The positional parameters of atom H1 were obtained from a difference map and refined with an isotropic displacement parameter. Selected bond distances and angles are given in Table 2. The molecular structure is shown in Fig. 2.

The molecular structure corresponds to the expected *trans* stereochemistry about the N11=N12 double bond. Free diaryltriazenes typically present a delocalization of the π electrons on the triazene group towards the terminal aryl substituents. This feature is supported by the deviations observed from normal N-N and C<sub>aryl</sub>-N bond lengths. The N11=N12 bond [1.257(8)Å] is longer than the characteristic value for a double bond (1.236 Å), whereas the N12-N13 bond [1.326(10)Å] is shorter than the characteristic value for a single bond (1.404 Å).<sup>3</sup> On the other hand, the C21-N13 [1.380(11)Å] and C11-N11 [1.437(10)Å] bonds are shorter than the characteristic N-C<sub>aryl</sub> single bonds (secondary amines, R<sub>2</sub>NH, R = Csp<sup>2</sup>; 1.452 Å).<sup>4</sup> These values are in good agreement with those observed in similar compounds: 1,3-bis(3-nitrophenyl)triazene [N=N = 1.261(2)Å and N-N = 1.326(2)Å],<sup>5</sup> 1,3-bis(2,4-dibromophenyl)triazene [N=N = 1.267(7)Å and N-N = 1.332(7)Å],<sup>6</sup> and *trans*-1-(4-chlorophenyl)-3-(4-nitrophenyl)-1-triazene, hereafter (II) [N=N = 1.262(2)Å and N-N = 1.341(2)Å].<sup>7</sup> The whole molecule is almost planar (r.m.s. deviation = 0.0945 Å). The molecular and crystal structures of (I) and (II) are analogous with each other. The dihedral angle [6.7(6)°] between the terminal phenyl rings is similar to that angle [5.8(2)°] found in (II). The bond angle of the N=N-N triad [N11-N12-N13 = 110.9(7)°] is very close to that angle found in (II) [111.9(2)°].

The crystal structure of (I) contains molecules related by the axial *c*-glide plane, generating an infinite one-dimensional linear chain along the [001] direction via N-H...O hydrogen bonds and C-H...O intermolecular interactions (Table 3). The molecules are associated through hydrogen bonds including a bifurcated acceptor geometry (D<sub>1</sub>-H<sub>1</sub>, D<sub>2</sub>-H<sub>2</sub>)...A (D = donor atom, A = acceptor atom), (N13-H1, C22-H22)...O12', and non-classical C15-H15...O11'' hydrogen bonds; symmetry codes: (') 1/2-x, 1-y, -1/2+z; (") x, y, -1+z. In comparison, the crystal structure of (II) show molecules related by a screw axis generating a zigzag chain via N3-H...O2 hydrogen bonds [N3...O2' = 2.947(2)Å and N3-H...O2' = 153.7(2)°; symmetry

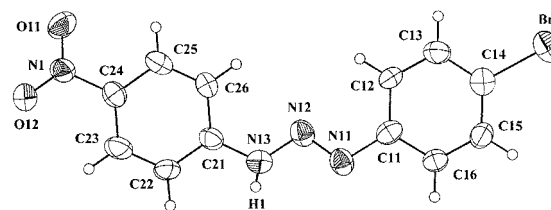


Fig. 2 Molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have arbitrary radii.

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

D-H...A	D-H	H...A	D...A	D-H...A
N13-H1...O12'	0.65(7)	2.32(8)	2.965(13)	174(9)
C15-H15...O11''	0.93	2.57	3.356(10)	143
C22-H22...O12'	0.93	2.55	3.309(10)	139

Symmetry codes: (') 1/2-x, 1-y, -1/2+z; (") x, y, -1+z

code: (') x+1/2, -y+3/2, -z]. Further, the crystal structure of (II) also shows C12-H...O2 intermolecular interactions [C12...O2' = 3.291(3)Å and C12-H...O2' = 138.9(3)°; symmetry code: (') x+1/2, -y+3/2, -z].

The phenyl rings C11-C16 (r.m.s. deviation 0.0044 Å) and C21-C26 (r.m.s. deviation 0.0044 Å) are planar within the experimental error, and make an interplanar angle of 8.0(4)°, which demonstrate that the whole molecule is almost planar.

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