

1,3-Bis(2,4-dibromophenyl)triazene

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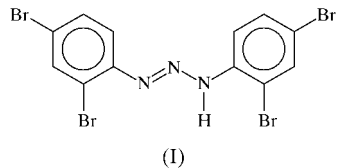
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The crystal structure of the title compound, C₁₂H₇Br₄N₃, shows that the stereochemistry about the N=N double bond of the N=N–N(H) moiety is *trans*. The whole molecule deviates slightly from planarity (r.m.s. deviation 0.164 Å). While one of the aryl substituents is almost coplanar with the triazene chain, weak intermolecular Br⋯C contacts cause the second aryl substituent to deviate by an angle of 9.1 (8)° from the plane defined by the N=N–N group. Weak intermolecular N–H⋯Br interactions between molecules related by the diagonal glide plane give rise to chains, which are stacked along the [100] crystallographic direction. An unequal distribution of double-bond character between the N atoms suggests a delocalization of π electrons over the diazoamino group and the adjacent aryl groups.

Comment

Free 1,3-disubstituted triazenes, RN=N–N(H)R, are generally believed to adopt a *trans* stereochemistry about the N=N double bond (Moore & Robinson, 1986). This arrangement has been confirmed for numerous examples characterized by X-ray diffraction. We report here the synthesis and structural characterization of the title compound, (I), a symmetric disubstituted 1,3-diaryltriazene having polarizable halogen atoms on the terminal aryl (ar) rings. These halogen atoms make contacts with the H atom of the protonated triazene chain.



The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Deviations from normal N–N and C_{ar}–N bond lengths suggest that the delocalization of the π electrons on the triazene group has

extended to the terminal aryl substituents. N1=N2 [1.267 (7) Å] is longer than the characteristic value for a double bond (1.24 Å), whereas N2–N3 [1.332 (7) Å] is shorter than the characteristic value for a single bond (1.44 Å) (*International Tables for X-ray Crystallography*, 1985, Vol. III, p. 270). Both N1–C11 [1.422 (7) Å] and N3–C31 [1.388 (8) Å] are shorter than expected for a C_{ar}–N single bond. These values are in good agreement with those found in related compounds (Zhang *et al.*, 1999; Walton *et al.*, 1991).

The terminal 2,4-dibromophenyl substituents make an interplanar angle of 14.7 (2)°, indicating the lack of planarity of the whole molecule. Due to the weak intramolecular N3–H3⋯Br3 interaction [N3⋯Br3 3.076 (5) Å], the related 2,4-dibromophenyl substituent is nearly coplanar with the N1=N2–N3 group [N2–N3–C31–C32 174.7 (6)°].

The crystal structure of (I) reveals that diagonal glide-plane-related molecules are ordered into chains by weak N3–H3⋯Br2 intermolecular interactions [N3⋯Br2ⁱ 3.717 (6) Å; symmetry code: (i) $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$]. These chains are stacked along the [100] direction, and are associated in pairs by an inversion centre. Weak interactions between these pairs can be recognized by intermolecular C⋯Br contacts [C16⋯Br1ⁱⁱ 3.788 (7) Å; symmetry code: (ii) $2 - x, 1 - y, 2 - z$]. On the other hand, weak intermolecular C⋯Br contacts [C13⋯Br3ⁱⁱⁱ 3.419 (6) Å and C14⋯Br3ⁱⁱⁱ 3.455 (7) Å; symmetry code: (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$] observed along the individual polymer chains hinder the coplanarity of the C11–C16 aryl group with the plane defined by the N1=N2–N3 group [interplanar angle 9.1 (8)°].

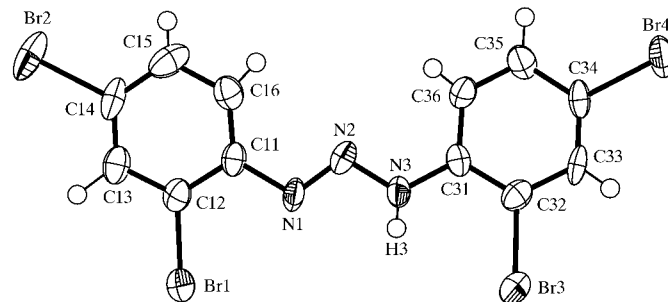


Figure 1

The molecular structure of (I) with 70% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Experimental

2,4-Dibromoaniline (5.02 g, 20.0 mmol) was dissolved in glacial acetic acid (40 ml) and cooled below room temperature. A sodium nitrite solution (0.69 g, 10 mmol) in water (10 ml) was added slowly with continuous stirring. A yellow precipitate was observed. After complete addition of the above solution, the resulting mixture was neutralized with a 10% aqueous solution of NaHCO₃. The yellow crude product was isolated by filtration and dried over P₂O₅ under vacuum. The product was recrystallized from a tetrahydrofuran–*n*-hexane mixture (1:1). Yellow plate-shaped crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of the solvent mixture (yield 6.35 g, 95%; m.p. 428–429 K).

Crystal data

C₁₂H₇Br₄N₃
M_r = 512.85
 Monoclinic, *P*2₁/*n*
a = 10.701 (5) Å
b = 9.949 (5) Å
c = 13.888 (5) Å
 β = 90.080 (5)
V = 1478.6 (11) Å³
Z = 4

D_x = 2.304 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 6.2–15.1°
 μ = 10.88 mm⁻¹
T = 293 (2) K
 Plate, yellow
 0.3 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (Spek, 1990)
T_{min} = 0.115, *T_{max}* = 0.337
 3358 measured reflections
 2878 independent reflections
 2045 reflections with *I* > 2σ(*I*)

R_{int} = 0.037
 θ_{\max} = 26°
h = -13 → 13
k = -12 → 1
l = 0 → 17
 3 standard reflections
 frequency: 60 min
 intensity variation: ±0.5%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.111
S = 1.02
 2878 reflections
 172 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0616P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.01 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.00 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Br3—C32	1.900 (7)	N2—N1	1.267 (7)
Br4—C34	1.892 (6)	N1—C11	1.422 (7)
Br1—C12	1.890 (6)	C13—Br3 ⁱ	3.419 (6)
Br2—C14	1.913 (6)	C14—Br3 ⁱ	3.455 (7)
N3—N2	1.332 (7)	C16—Br1 ⁱⁱ	3.788 (7)
N3—C31	1.388 (8)		
N2—N3—C31	120.2 (5)	C35—C34—Br4	119.3 (5)
N1—N2—N3	111.6 (5)	C12—C11—N1	117.3 (6)
N2—N1—C11	112.9 (5)	C11—C12—Br1	120.8 (4)
N3—C31—C32	120.7 (6)	C13—C14—Br2	118.9 (5)
C31—C32—Br3	119.5 (5)		
C31—N3—N2—N1	177.7 (5)	N2—N1—C11—C16	-7.8 (9)
N3—N2—N1—C11	177.9 (5)	N2—N1—C11—C12	172.9 (6)
N2—N3—C31—C32	174.7 (6)	N1—C11—C12—Br1	-2.4 (8)
N2—N3—C31—C36	-3.9 (9)	N2—N3—C31—C32	174.7 (6)
N3—C31—C32—Br3	-0.4 (8)		

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $2 - x, -y, -z$.

Table 2

Hydrogen-bonding geometry and short intermolecular contacts (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3...Br2 ⁱ	0.86	2.91	3.717 (6)	156
N3—H3...Br3	0.86	2.64	3.076 (5)	113

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

H atoms were treated as riding, with C—H = 0.93 Å, N—H = 0.86 Å and *U*_{iso}(H) = 1.2*U*_{eq} of the parent atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* in *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97* and *ORTEP-32*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1213). Services for accessing these data are described at the back of the journal.

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