# 3-(4-Acetylphenyl)-1-(4-nitrophenyl)-triazene

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The crystal structure of the title compound, $C_{14}H_{12}N_4O_3$, shows that the stereochemistry about the N=N double bond of the N=N—N(H) moiety is *trans*. The whole molecule is almost planar (r.m.s. deviation = 0.0654 Å), the interplanar angle between the phenyl rings being 0.7 (1)° and the largest interplanar angle being that between the phenyl ring and the nitro group of the 4-nitrophenyl substituent [11.5 (2)°]. Intermolecular N—H⋯O interactions between molecules related by translation give rise to chains along the [110] and [1$\bar{1}$0] directions, and these chains are held together by N⋯O $\pi$–$\pi$ interactions. An unequal distribution of the double-bond character among the N atoms suggests a delocalization of $\pi$ electrons over the diazoamine group and the adjacent aryl substituents.

## Comment

Numerous examples of free 1,3-disubstituted triazenes, $R$N=N—N(H)$R$ ($R$ is an aryl or alkyl group), characterized by X-ray diffraction studies, have confirmed a *trans* stereochemistry about the N=N double bond (Moore & Robinson, 1986). On the other hand, free 1,3-diaryltriazenes show that the N=N—N(H) moiety is able to support intermolecular interactions by hydrogen bonding with polarizable atoms of the terminal aryl rings, giving rise to infinite chains that are commonly associated by weak interactions. As part of a study of intermolecular hydrogen-bonding interactions in the solid state of asymmetric disubstituted 1,3-diaryltriazenes having $\pi$ acid groups on the terminal aryl rings, we report here the structure of the title compound, (I).

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. A typical feature of free diaryltriazenes is the delocalization of the $\pi$ electrons on the triazene group, extending to the terminal aryl substituents. This observation is supported by the deviations from normal N—N and $C_{aryl}$—N bond lengths. The N11=N12 bond [1.267 (2) Å] is longer than the characteristic value for a

double bond (1.236 Å), whereas the N12—N13 bond [1.322 (2) Å] is shorter than the characteristic value for a single bond (1.404 Å; Allen *et al.*, 1987; Teatum *et al.*, 1960). The C21—N13 [1.392 (3) Å] and C11—N11 bonds [1.416 (3) Å] are shorter than expected for N—$C_{aryl}$ single bonds (secondary amines, NH$R_2$, $R$ = C$sp^2$; 1.452 Å; Orpen *et al.*, 1989). These values are in good agreement with those found in the related compounds 1,3-bis(3-nitrophenyl)triazene [N=N = 1.261 (2) Å and N—N = 1.326 (2) Å; Zhang *et al.*, 1999] and 1,3-bis(4-acetylphenyl)triazene [N=N = 1.267 (4) Å and N—N = 1.329 (3) Å; Walton *et al.*, 1991].



(I)
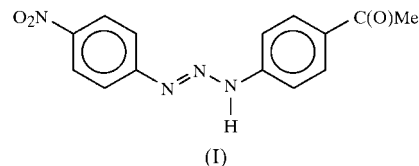
The crystal structure contains molecules related by translation, which form chains along the [110] and [1$\bar{1}$0] directions *via* N—H⋯O hydrogen bonds [N13⋯O1i = 2.880 (3) Å and
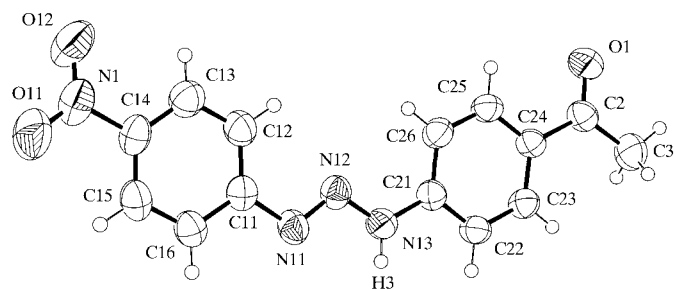


**Figure 1**
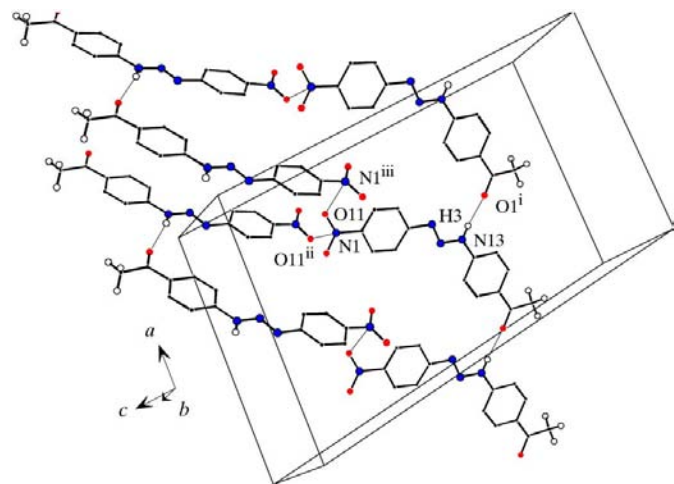The molecular structure of (I), shown with 50% probability displacement ellipsoids for non-H atoms.



**Figure 2**
The unit cell of (I) in a view inclined towards [010] and [001]. The N—H⋯O hydrogen bonds and transmolecular N⋯O $\pi$–$\pi$ interactions are shown as thin lines. [Symmetry codes: (i) $\frac{1}{2}+x$, $-\frac{1}{2}+y$, $z$; (ii) $\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (iii) $\frac{3}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$.]

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# organic compounds

N13—H3···O1$^i$ = 158 (2)°; symmetry code: (i) $\frac{1}{2} + x$, $-\frac{1}{2} + y$, $z$]. These chains are held together by N···O $\pi$–$\pi$ interactions [N1···O11$^{ii}$ = 3.317 (3) Å    and    O11···N1$^{iii}$ = 3.317 (3) Å; symmetry codes: (ii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (iii) $\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$; Fig. 2]. On the other hand, these weak intermolecular N···O $\pi$–$\pi$ contacts hinder the coplanarity of the O11/N1/O12 nitro group with the C11–C16 phenyl ring [the interplanar angle is 11.5 (2)°]. The phenyl rings are planar within experimental error (r.m.s. deviation 0.0032 Å) and make an interplanar angle of 0.7 (1)°, indicating that the whole molecule is almost planar.

## Experimental

4-Nitroaniline (2.76 g, 20.0 mmol) was dissolved in a 50% aqueous solution of HCl (40 ml) and cooled to 270–273 K. A sodium nitrite solution (1.37 g, 20.0 mmol) in water (20 ml) was added slowly with continuous stirring. A solution of 4-acetylaniline (2.70 g, 20.0 mmol) in glacial acetic acid (40 ml) was added slowly to the reaction mixture. Stirring was continued for 2 h (at a temperature below 268 K). The resulting mixture was neutralized with a 10% aqueous solution of NaHCO$_3$. The crude orange product was isolated by filtration and dried over P$_2$O$_5$ under vacuum. The product was recrystallized from a tetrahydrofuran/$n$-hexane mixture (1:1). Orange bar-shaped crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation of the solvent mixture (yield 5.12 g, 90%; m.p. 433–434 K).

### Crystal data

C$_{14}$H$_{12}$N$_4$O$_3$
$M_r$ = 284.28
Monoclinic, $C2/c$
$a$ = 14.357 (6) Å
$b$ = 7.1964 (13) Å
$c$ = 26.779 (5) Å
$\beta$ = 100.35 (4)°
$V$ = 2721.7 (13) Å$^3$
$Z$ = 8

$D_x$ = 1.388 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 10.2–24.0°
$\mu$ = 0.10 mm$^{-1}$
$T$ = 293 (2) K
Bar, orange
0.40 × 0.40 × 0.25 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega$ scans
3468 measured reflections
3266 independent reflections
1809 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.015

$\theta_{max}$ = 28.0°
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 9$
$l = -1 \rightarrow 35$
3 standard reflections
 frequency: 60 min
 intensity decay: <1%

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.142
$S$ = 1.01
3266 reflections
195 parameters

H atoms treated by a mixture of independent and constrained refinement
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$

H atoms of the phenyl and methyl groups were positioned geometrically (C—H = 0.93 Å for C$sp^2$ and 0.96 Å for C$sp^3$ atoms) and treated as riding on their respective C atoms, with $U_{iso}$(H) values set at 1.2$U_{eq}$(C$sp^2$) and 1.5$U_{eq}$(C$sp^3$). The positional parameters of

**Table 1**
Selected geometric parameters (Å, °).

| O1—C2 | 1.219 (2) | N11—N12 | 1.267 (2) |
|---|---|---|---|
| O11—N1 | 1.222 (3) | N12—N13 | 1.322 (2) |
| O12—N1 | 1.223 (3) | | |
| | | | |
| N12—N11—C11 | 112.07 (17) | O1—C2—C24 | 120.52 (19) |
| N11—N12—N13 | 111.74 (17) | C24—C2—C3 | 120.30 (19) |
| N12—N13—C21 | 121.09 (19) | | |

atom H3 were obtained from a difference map and refined with an isotropic displacement parameter. The methyl group was refined as a rigid group, with the rotation around the C2—C3 bond as a free variable. The nitro O atoms and the acetyl O atom have elongated displacement ellipsoids (Fig. 1). Split peaks for these atoms were not observed and consequently a disorder model was not used in the refinement.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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