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1,3-Bis(4-methylphenyl)triazene, 1-(4-chlorophenyl)-3-(4-fluorophenyl)-triazene and 1-(4-fluorophenyl)-3-(4-methylphenyl)triazene

Nevzat Karadayı,[a]* Şükriye Çakmak,[b] Mustafa Odabaşoğlu[b] and Orhan Büyükgüngör[c]

[a]Industrial Electronics Program, Samsun Vocational School of Higher Education, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, [b]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, and [c]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Samsun, Turkey
Correspondence e-mail: nevzatk@omu.edu.tr

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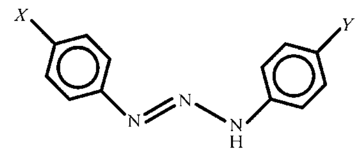
The title 4,4′-disubstituted diphenyl-1,3-triazines, $C_{14}H_{15}N_3$, (I), $C_{12}H_9ClFN_3$, (II), and $C_{13}H_{12}FN_3$, (III), each contain a triazene group (–N═N—NH–) having an extended conformation. The dihedral angles between the two benzene rings in (I), (II) and (III) are 4.3, 3.4 and 6.5°, respectively. The molecules are almost entirely planar, with maximum deviations from the mean planes of 0.1087 (2), −0.1072 (7) and 0.1401 (3) Å, respectively. In each compound, the molecules are linked by N—H···N hydrogen bonds to form chains and pack similarly in the crystal structures.

Comment

Triazene compounds containing a diazoamine group have important industrial and medical applications. The substituted triazenes (*R*N═N—NH–) find wide-ranging applications as initiators of radical polymerization (Rapta *et al.*, 1996), as efficient chelating agents (Leman *et al.*, 1992; Cotton *et al.*, 1992) and as antitumor drugs (Wilman, 1988). These compounds, characterized by having a diazoamine group, commonly adopt the *trans* configuration in the ground state. They are also known to undergo reversible changes in double-bond configuration as a result of photoinduced and thermally induced *trans–cis–trans* isomerization (Baro *et al.*, 1983; Le Fevre & Liddicoet, 1951; Barra & Chen, 2000). Photochromic materials of this type are of interest for potential applications, among others, in molecular electronic devices (Martin *et al.*, 1995). The results of the present X-ray analysis are in agreement with those of the structure analyses of similar substituted triazenes (Anulewicz, 1997; Zhang *et al.*, 1999; Hörner *et al.*, 2004, 2002). In this paper, we report the structures of the three title 4,4′-disubstituted diphenyl-1,3-triazines.

1,3-Bis(4-methylphenyl)triazene, (I), 1-(4-chlorophenyl)-3-(4-fluorophenyl)triazene, (II), and 1-(4-fluorophenyl)-3-(4-methylphenyl)triazene, (III), differ only in the substituents at atoms C4 and C10; these substituents are methyl groups in (I), Cl and F atoms in (II), and a methyl group and an F atom in (III). The angle between the benzene rings is 4.28 (1)° for (I), 3.42 (4)° for (II) and 6.53 (2)° for (III). These angles are in close agreement with the value observed in another open-ring intermediate in the synthesis of triazane [6.2 (2)°; Zhang *et al.*, 1999].



(I) $X=Y=CH_3$
(II) X=F, Y=Cl
(III) $X=CH_3$, Y=F

The molecular structures of (I), (II) and (III) are shown in Fig. 1, and the geometric parameters are compared in Table 1. For (I), within the limits of uncertainty, the bond lengths and angles of the two methylphenyl rings are in agreement with one another. The N3═N2 bond is longer than the value expected for a double bond, the N2—N1 bond is shorter than expected for a single bond, and the C1—N1 and C7—N3 bonds are both short for single C_{ar}—N bonds. These values (Table 1) are in good agreement with those found in related

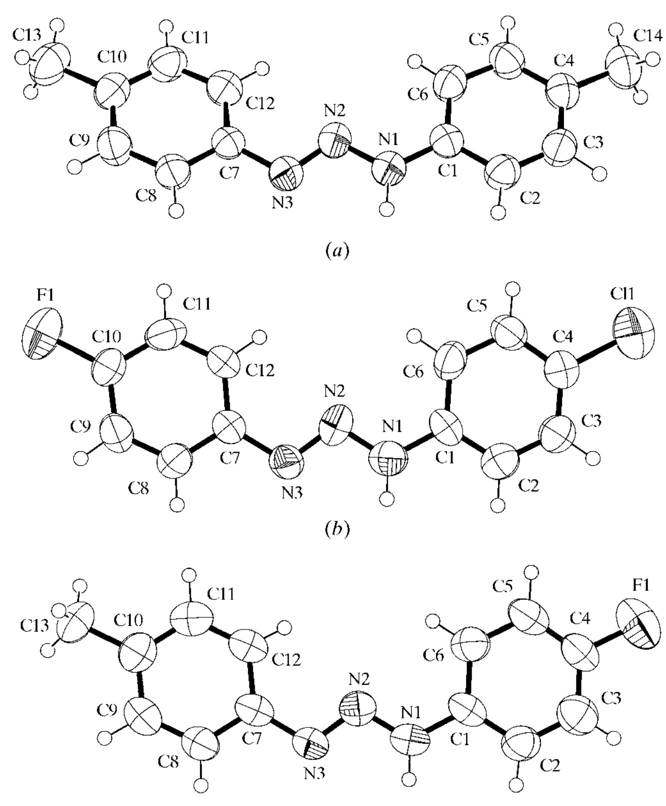


Figure 1
ORTEP-3 (Farrugia, 1997) drawings of the title compounds, showing the atomic numbering schemes and 50% probability displacement ellipsoids for (*a*) (I), (*b*) (II) and (*c*) (III).

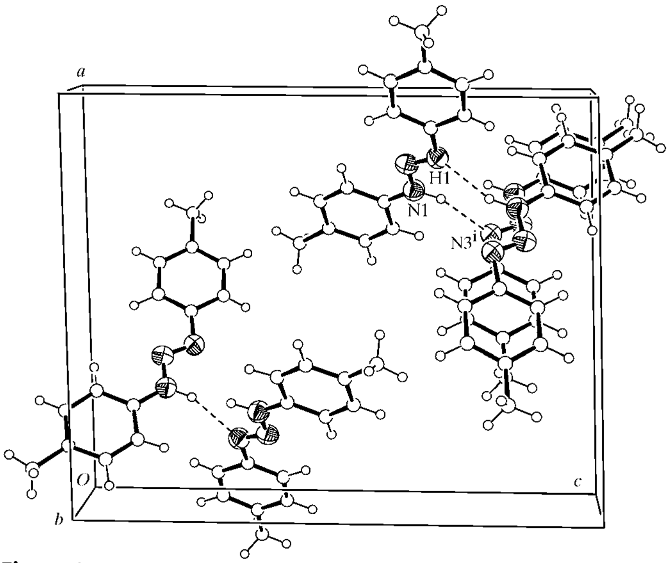


Figure 2
A perspective view of the packing in (I). The relationship between the molecules in (II) and (III) is similar. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

compounds (Anulewicz, 1997; Walton *et al.*, 1991; Zhang *et al.*, 1999). The dihedral angles between the two benzene rings and the C1—N1—N2—N3 and N1—N2—N3—C7 torsion angles are 177.21 (15) and 177.97 (14)°, respectively, showing the near coplanarity of the whole molecule. The crystal structure of (I) has been reported by Kondrashev (1964). [The *b* axis of the monoclinic cell lies along the axis of the needle-shaped crystals. The development of the four planes *hkl* (*k* = 0–3) and of the planes *hk*0 was obtained with a Weissenberg goniometer, and from these the space group $P2_1/n$ was established. From the rotation X-ray photograph and the development of *h*0*l*, taken with NaCl as standard, the following lattice parameters were determined: *a* = 17.83 (2) Å, *b* = 4.83 (1) Å, *c* = 14.40 (2) Å and β = 88.40 (10)°.] The molecular structures of (II) and (III) are similar to that of (I), with small differences for some bond lengths due to the presence of the F and Cl atoms attached to the benzene rings (Figs. 1*b* and 1*c*). The N3═N2 bond lengths [1.2777 (17) Å in (I) and 1.280 (3) Å in (III)] are somewhat shorter than the value of 1.317 (8) Å in (II).

Molecules of (I), (II) and (III) pack similarly in the unit cell, as shown in Fig. 2, and all have intermolecular N—H···N hydrogen bonds (Table 2). These hydrogen bonds are somewhat longer than the analogous interaction in the spiral of the β modification of 3-(4-bromophenyl)-1-phenyltriazine, (IV) (3.206 Å; Omel'chenko & Kondrashev, 1973). This difference is due to the different packing characters, where in the case of the flat parallel molecules the smallest N—H···N distance should be 3.60 Å. The shortening is achieved as a result of strong bending of the molecules of (IV), which form dimers in which the molecules are bent towards one another, and of the deviation of the N atoms from the plane of the molecule to the same side; this configuration provides additional evidence for the existence of strong interaction between the molecules in the dimer (Omel'chenko & Kondrashev, 1973).

Experimental

Compounds (I) (m.p. 388–389 K), (II) (m.p. 402–403 K) and (III) (m.p. 385–386 K) were prepared as described by Hörner *et al.* (2004) using 4-methylaniline, 4-fluoroaniline and 4-chloroaniline as starting materials. The products were recrystallized from tetrahydrofuran (THF) and well shaped crystals were obtained by slow evaporation of an *n*-hexane/THF (1:1 *v*/*v*) solution.

Compound (I)

Crystal data

$C_{14}H_{15}N_3$	D_x = 1.209 Mg m^{-3}
M_r = 225.29	Mo *K*α radiation
Monoclinic, $P2_1/n$	Cell parameters from 3402
a = 14.4024 (19) Å	θ = 1.8–28.6°
b = 4.8171 (4) Å	μ = 0.07 mm^{-1}
c = 17.840 (2) Å	*T* = 296 (2) K
β = 91.510 (11)°	Plate, light brown
V = 1237.3 (3) Å^3	0.44 × 0.29 × 0.09 mm
Z = 4	

Data collection

Stoe IPDS-II diffractometer	2184 independent reflections
ω scans	1091 reflections with $I > 2\sigma(I)$
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	θ_{max} = 25.0°
T_{min} = 0.976, T_{max} = 0.994	*h* = −17 → 17
2184 measured reflections	*k* = 0 → 5
	l = 0 → 21

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.033	$(\Delta/\sigma)_{max}$ = 0.003
$wR(F^2)$ = 0.066	$\Delta\rho_{max}$ = 0.10 e Å^{-3}
S = 0.99	$\Delta\rho_{min}$ = −0.10 e Å^{-3}
2184 reflections	Extinction correction: *SHELXL97*
194 parameters	Extinction coefficient: 0.0063 (11)
H atoms treated by a mixture of independent and constrained refinement	

Compound (II)

Crystal data

$C_{12}H_9ClFN_3$	D_x = 1.353 Mg m^{-3}
M_r = 249.67	Mo *K*α radiation
Monoclinic, $P2_1/n$	Cell parameters from 4244 reflections
a = 14.500 (3) Å	θ = 1.8–24.4°
b = 4.7385 (5) Å	μ = 0.30 mm^{-1}
c = 17.848 (3) Å	*T* = 296 (2) K
β = 92.298 (16)°	Plate, brown
V = 1225.3 (4) Å^3	0.50 × 0.29 × 0.06 mm
Z = 4	

Data collection

Stoe IPDS-II diffractometer	978 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.078
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	θ_{max} = 25.0°
T_{min} = 0.886, T_{max} = 0.981	*h* = −17 → 17
8654 measured reflections	*k* = −5 → 5
2157 independent reflections	*l* = −21 → 21

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.087	$w = 1/[\sigma^2(F_o^2) + (0.1152P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.253	$(\Delta/\sigma)_{max}$ < 0.001
S = 1.08	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
2157 reflections	$\Delta\rho_{min}$ = −0.44 e Å^{-3}
154 parameters	

Compound (III)

Crystal data

$C_{13}H_{12}FN_3$
M_r = 229.26
Monoclinic, $P2_1/n$
a = 13.683 (3) Å
b = 4.7712 (6) Å
c = 17.742 (4) Å
β = 92.512 (18)°
V = 1157.2 (4) Å^3
Z = 4
D_x = 1.316 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3288 reflections
θ = 1.8–27.7°
μ = 0.09 mm^{-1}
T = 296 (2) K
Plate, brown
0.50 × 0.28 × 0.06 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
6441 measured reflections
2019 independent reflections
757 reflections with $I > 2\sigma(I)$
R_{int} = 0.081
θ_{max} = 25.0°
$h = -16 \rightarrow 16$
$k = -5 \rightarrow 5$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.110
S = 0.85
2019 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Comparative selected geometric parameters (Å, °).

	(F)[a]	(I)	(II)	(III)
N1—N2	1.334 (4)	1.332 (2)	1.321 (7)	1.316 (3)
C1—C2	1.378 (4)	1.375 (2)	1.359 (10)	1.370 (4)
C1—C6	1.399 (5)	1.390 (2)	1.415 (10)	1.408 (4)
C7—C8	1.386 (5)	1.366 (2)	1.361 (9)	1.372 (4)
C7—C12	1.385 (5)	1.381 (2)	1.388 (9)	1.400 (4)
C4—C14	–	1.507 (2)	–	–
C10—C13	–	1.516 (2)	–	1.483 (4)
Cl1—C4	–	–	1.731 (7)	–
N2—N1—C1	119.0 (3)	120.35 (17)	119.2 (6)	121.4 (3)
N3—N2—N1	112.9 (2)	112.07 (15)	110.9 (6)	112.4 (3)
N2—N3—C7	111.9 (3)	112.65 (14)	111.8 (5)	112.1 (2)
C2—C1—N1	118.6 (3)	118.56 (17)	119.3 (7)	119.9 (3)
N1—C1—C6	121.1 (3)	122.71 (18)	122.1 (7)	120.6 (3)
C8—C7—N3	115.9 (3)	115.97 (17)	116.5 (6)	117.0 (3)
C12—C7—N3	125.0 (3)	125.41 (18)	126.4 (6)	126.5 (3)
N1—C1—C2—C3	179.9 (3)	177.64 (18)	176.8 (7)	178.4 (3)
N3—C7—C8—C9	179.1 (3)	179.17 (17)	178.7 (6)	179.7 (3)
N1—N2—N3—C7	178.8 (3)	177.97 (14)	177.5 (5)	178.3 (3)
C1—N1—N2—N3	179.0 (3)	177.21 (15)	177.5 (5)	177.9 (3)

Note: (*a*) 1,3-bis(*p*-fluorophenyl)triazine (Anulewicz, 1997).

For (I), the methyl H atoms were refined using a riding model, with fixed C—H distances of 0.96 Å [U_{iso}(H) = 1.5U_{eq}(C)]. All other H atoms were refined freely [C—H = 0.922 (17)–1.001 (19) Å and U_{iso}(H) = 0.063 (6)–0.096 (7) Å^2]. For (II), all H atoms were refined using a riding model, with fixed C—H distances of 0.93 Å [U_{iso}(H) = 1.2U_{eq}(C,N)]. For (III), the methyl H atoms and those attached to atoms C3 and N1 were refined with fixed displacement parameters [U_{iso}(H) = 1.5U_{eq}(methyl C) and 1.2U_{eq}(C,N)] using a riding model (methyl C—H = 0.96 Å and C3—H3 = 0.93 Å). All other H atoms were refined freely [C—H = 0.88 (3)–0.97 (3) Å and U_{iso}(H) = 0.063 (9)–0.116 (14) Å].

Table 2
Hydrogen-bonding geometry (Å, °).

	D—H···A	D—H	H···A	D···A	D—H···A
(I)	N1—H1···N3^{i}	0.99 (2)	2.31 (2)	3.242 (2)	158.1 (15)
(II)	N1—H1···N3^{i}	0.86	2.39	3.223 (8)	163
(III)	N1—H1···N3^{i}	0.86	2.38	3.211 (3)	164

Symmetry code: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$.

For all three compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLUTON* (Spek, 1997); publication software: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1464). Services for accessing these data are described at the back of the journal.

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