

***p*-(3,3-Dimethyl-1-triazeno)benzotrile**

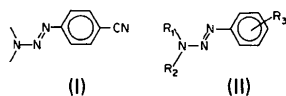
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Abstract. C₉H₁₀N₄, *M_r* = 174.21, monoclinic, *P*2₁/*c*, *a* = 5.863 (2), *b* = 7.656 (1), *c* = 21.187 (3) Å, β = 94.92 (2)°, *V* = 947.5 (3) Å³, *Z* = 4, *D_x* = 1.221 g cm⁻³ at 295 (1) K, λ(Cu *K*α) = 1.54184 Å, μ = 6.0 cm⁻¹, *F*(000) = 368, 1956 unique reflections measured, final *R* = 0.037 for 1652 reflections with *I* > 3.0σ(*I*). The triazeno moiety is twisted 10.9 (3)° and bent down 2.1 (2)° from the mean plane of the benzene ring, but is otherwise no different from other phenyltriazenes. However, the benzene ring shows significant deviation from planarity toward a twist-boat conformation. There is also 'quinoidal' shortening of the aromatic bonds, indicating significant through-resonance of the triazeno and *para*-cyano groups.

Introduction. DTIC, 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide, has been widely used to treat malignant melanoma. When attached to aromatic rings, the 3,3-dimethyl-1-triazeno moiety [-N=NN(CH₃)₂] has also yielded compounds having antitumor activity (Hatheway, Hansch, Kim, Milstein, Schmidt, Smith & Quinn, 1978; Denny, Cain, Atwell, Hansch & Leo, 1982). In addition, the carcinogenicity and mutagenicity of the triazenes have been studied (Venger, Hansch, Hatheway & Amrein, 1979). We report herein the structure determination of the title compound (I), which was undertaken in order to obtain reliable coordinates for molecular-orbital calculations to be used in a structure-activity analysis of substituted 1-phenyl-3,3-dimethyltriazenes (II).



Experimental. A light beige tabular crystal, grown by slow evaporation from acetonitrile, 0.05 × 0.30 × 0.30 mm, mounted on a glass fiber in random orientation on an Enraf-Nonius CAD-4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal incident-beam monochromator, λ(Cu *K*α) = 1.54184 Å. Cell constants from 25 reflections, 20 <

θ < 25°. Space group determined to be *P*2₁/*c* from systematic absences.

Data were collected (*h* = -7 to 7, *k* = 0 to 9, *l* = -26 to 26) using ω-2θ scans, variable scan rate 1-4° min⁻¹, to a maximum 2θ of 150°. Equivalent intensities averaged, *R* = 0.021 for 3157 reflections, 1956 of which were unique. Three representative reflections (300, 040, 002) were measured every 166 minutes, and these showed a total intensity loss of 1.6%; thus, a linear decay correction was applied ranging from 1.000 to 1.008. Lorentz and polarization corrections were applied. An empirical absorption correction, based on a series of ψ scans, yielded relative transmission coefficients ranging from 0.928 to 0.997. A secondary-extinction correction was applied and refined in least squares to 3.6 (4) × 10⁻⁶ (absolute units).

Structure solution by *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), and successive difference Fourier syntheses. All atoms, including H atoms, were located and included in the refinement. The structure was refined by weighted full-matrix least squares using two different programs: *SHELX76* (Sheldrick, 1976) and *SDP/VAX* (Frenz, 1978). Both programs refined the same unconstrained model in which anisotropic thermal parameters were varied for all atoms except H atoms, which retained variable isotropic thermal parameters. The final models from the two least-squares programs were essentially identical, with all geometric and thermal parameters and their variances agreeing within the limits of error. The results from *SHELX76* are cited below.

The function minimized was Σw(|*F_o*| - |*F_c*|)², and weights were assigned as w⁻¹ = σ(*F*)² + *pF*², where *p* was a variable which refined to 0.0019. Scattering factors, including anomalous dispersion, from *International Tables for X-ray Crystallography* (1974). 1652 reflections having *I* > 3σ(*I*) used in refinement. The final cycle included 159 variables and converged (largest Δ/σ = 0.02) to *R* = 0.037, *wR* = 0.065, *R*(all) = 0.049, and *S* = 1.22. There were no correlation coefficients greater than 0.50, and the maximum and minimum residual electron densities were 0.19 (2) and -0.10 (2) e Å⁻³. Other programs used were *ORTEP* (Johnson, 1965) and *PLUTO78* (Motherwell & Clegg, 1978).

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Table 1. Positional parameters and their *e.s.d.*'s

	x	y	z	B _{eq} (Å ²)
N1	0.6000 (2)	0.8866 (1)	0.28316 (4)	4.32 (2)
N2	0.7040 (2)	0.8372 (1)	0.33515 (4)	4.34 (2)
N3	0.5858 (2)	0.8543 (1)	0.38487 (4)	4.85 (2)
N4	1.2253 (2)	0.8261 (2)	0.02953 (5)	7.03 (3)
C1	0.7374 (2)	0.8648 (1)	0.23180 (4)	3.87 (2)
C2	0.6564 (2)	0.9436 (1)	0.17498 (5)	4.40 (2)
C3	0.7797 (2)	0.9350 (2)	0.12241 (5)	4.56 (2)
C4	0.9881 (2)	0.8469 (1)	0.12624 (5)	4.28 (2)
C5	1.0695 (2)	0.7658 (1)	0.18274 (5)	4.60 (2)
C6	0.9450 (2)	0.7734 (1)	0.23496 (5)	4.43 (2)
C7	0.7081 (3)	0.8174 (3)	0.44555 (6)	6.39 (4)
C8	0.3617 (3)	0.9333 (2)	0.38129 (7)	6.14 (3)
C9	1.1200 (2)	0.8358 (2)	0.07215 (5)	5.11 (3)
H2	0.502 (3)	1.005 (2)	0.1739 (6)	5.5 (3)*
H3	0.729 (3)	0.994 (2)	0.0824 (7)	6.6 (3)*
H5	1.228 (3)	0.706 (2)	0.1871 (7)	6.4 (3)*
H6	1.008 (3)	0.719 (2)	0.2724 (8)	5.8 (3)*
H7A	0.861 (4)	0.769 (3)	0.4394 (9)	8.3 (5)*
H7B	0.616 (4)	0.742 (3)	0.467 (1)	9.7 (5)*
H7C	0.725 (4)	0.924 (3)	0.469 (1)	11.3 (7)*
H8A	0.299 (4)	0.912 (3)	0.420 (1)	8.7 (5)*
H8B	0.267 (4)	0.874 (3)	0.344 (1)	9.7 (5)*
H8C	0.371 (5)	1.054 (4)	0.371 (1)	11.3 (7)*

Starred atoms were refined isotropically. The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation

$$\frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha].$$

Table 2. Bond lengths (Å), bond angles (°) and torsion angles (°)

N1-N2	1.270 (1)	C1-C6	1.401 (1)
N1-C1	1.418 (1)	C2-C3	1.380 (2)
N2-N3	1.316 (1)	C3-C4	1.392 (2)
N3-C7	1.445 (2)	C4-C5	1.396 (1)
N3-C8	1.442 (2)	C4-C9	1.439 (2)
N4-C9	1.139 (2)	C5-C6	1.378 (2)
C1-C2	1.393 (1)		
N2-N1-C1	111.62 (8)	C1-C2-C3	120.9 (1)
N1-N2-N3	114.68 (9)	C2-C3-C4	119.6 (1)
N2-N3-C7	115.9 (1)	C3-C4-C5	120.0 (1)
N2-N3-C8	122.7 (1)	C3-C4-C9	120.8 (1)
C7-N3-C8	120.6 (1)	C5-C4-C9	119.3 (1)
N1-C1-C2	116.00 (9)	C4-C5-C6	120.3 (1)
N1-C1-C6	124.78 (8)	C1-C6-C5	120.04 (9)
C2-C1-C6	119.21 (9)	N4-C9-C4	179.5 (1)
C1-N1-N2-N3	179.87 (11)	C2-C1-C6-C5	1.61 (15)
N2-N1-C1-C2	-168.82 (09)	C1-C2-C3-C4	-0.21 (16)
N2-N1-C1-C6	10.32 (14)	C2-C3-C4-C5	0.95 (17)
N1-N2-N3-C7	-173.44 (12)	C2-C3-C4-C9	179.92 (14)
N1-N2-N3-C8	-3.78 (16)	C3-C4-C5-C6	-0.40 (16)
N1-C1-C2-C3	178.13 (10)	C9-C4-C5-C6	-179.38 (11)
C6-C1-C2-C3	-1.06 (15)	C4-C5-C6-C1	-0.89 (16)
N1-C1-C6-C5	-177.50 (10)		

Discussion. Final positional and equivalent isotropic thermal parameters of (I) are shown in Table 1, and bond lengths, bond angles and torsion angles are shown in Table 2.* The molecule and the numbering scheme

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51057 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

used are shown in Fig. 1, and the unit cell is shown in Fig. 2.

Comparison of (I) with previously determined structures of type (II) (Kondrashev, 1974; Edwards, Chapuis, Templeton & Zalkin, 1977; Lunazzi, Cerioni, Foresti & Macciantelli, 1978; Mackay, McIntyre & Taylor, 1982; Randall & Schwalbe, 1984) shows that the bond distances, bond angles and torsion angles involving the triazene are all very similar (Table 3), even when hydrogen bonding occurs (Edwards *et al.*, 1977).

There are small but statistically significant distortions of the benzene ring. It is non-planar ($\chi^2 = 192$), with a maximum deviation from the mean plane of 0.010 (1) Å. The intra-annular torsion angles are diagnostic of a twist-boat conformation. A similar trend toward twist-boat was observed in *p*-cyanoaniline (Merlino & Sartori, 1982). This is in contrast to *p*-benzoquinone, which has a chair conformation at low temperature (van Bolhuis & Kiers, 1978).

p-Cyanoaniline (Merlino & Sartori, 1982) and *p*-nitroaniline (Colapietro, Domenicano, Marciante & Portalone, 1982) both display significant 'quinoidal' shortening. In (I), the average length of bonds C2-C3 and C5-C6 [1.379 (1) Å] is also significantly less than the average of the other four bonds [1.396 (1) Å]. This effect has been treated theoretically (Domenicano, Vaciago & Coulson, 1975; Hiberty & Ohanessian, 1984). There is thus significant through-resonance when the triazene function is conjugated with a strong electron acceptor. Kazitsyna, Ustynyuk, Gurman, Pergushov & Gruzdnova (1977) showed that through-

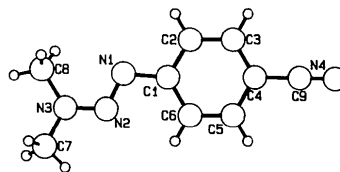
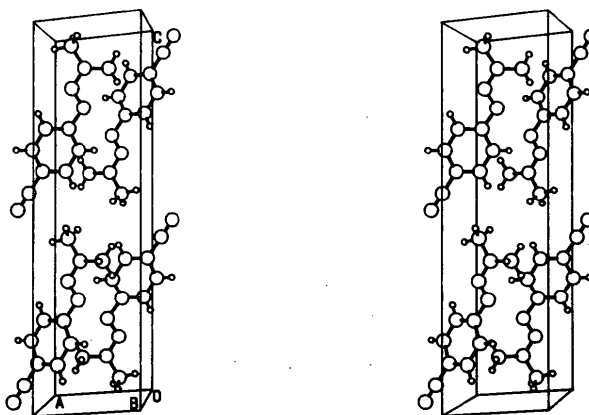
Fig. 1. View of a molecule of C₉H₁₀N₄.

Fig. 2. Stereoview of the unit cell.

Table 3. Comparison of geometries ($\text{\AA},^\circ$) of selected phenyltriazenes

	(I)	(III)	(IV)	(V)	(VI)	(VII)	Average
C1-N1	1.42	1.43	1.43	1.42	1.43	1.42	1.425 (5)
N1-N2	1.27	1.26	1.28	1.26	1.24	1.28	1.27 (1)
N2-N3	1.32	1.35	1.31	1.34	1.38	1.32	1.34 (2)
N3-C7	1.45	—	1.46	1.45	—	—	—
N3-C8	1.44	—	1.44	1.45	—	—	1.45
C2-C1-N1	116	113	118	115	115	117	116 (2)
C6-C1-N1	125	124	121	125	125	125	124 (2)
C1-N1-N2	112	114	111	112	113	112	112 (1)
N1-N2-N3	115	110	113	114	112	115	113 (2)
N2-N3-C7	116	121	115	112	120	—	—
N2-N3-C8	123	—	123	122	119	124	—
C7-N3-C8	121	—	120	123	118	—	—
C2-C1-N1-N2	-169	-177	-165	-172	-179	-159	—
C6-C1-N1-N2	10	1	16	7	1	22	—
C1-N1-N2-N3	180	179	179	176	180	180	—
N1-N2-N3-C7	-173	-179	-178	-170	173	—	—
N1-N2-N3-C8	-4	—	-0	-3	5	-10	—

(I) This work; (III) *p*-nitrodiazooaminobenzene (Kondrashev, 1974); (IV) 2-(3,3-dimethyltriazeno)phenyl-1-carboxamide (Edwards *et al.*, 1977); (V) (2,6-*cis*-dimethylpiperidyl)diazobenzene (Lunazzi *et al.*, 1978); (VI) 1,6-bis(*p*-chlorophenyl)-3,4-diacetylhexaaza-1,5-diene (MacKay *et al.*, 1982); (VII) 3-methyl-1-*p*-tolyltriazene (Randall & Schwalbe, 1984).

resonance is strongly correlated with the Hammett constant σ^+ , a significant parameter in quantitative structure-activity relationships of triazenes in mutagenesis (Venger *et al.*, 1979) and antitumor activity (Hatheway *et al.*, 1978).

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Structure of 2-Bromo-4-(2-chlorophenyl)-6*H*-thieno[3,2-*f*][1,2,4]triazolo-[4,3-*a*][1,4]diazepine (I) and of its 9-Cyclohexyl Derivative (II)*

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Abstract. (I) $C_{14}H_8BrClN_4S$, $M_r = 379.7$, monoclinic, $P2_1/c$, $a = 12.385$ (2), $b = 8.674$ (1), $c = 14.335$ (2) \AA , $\beta = 104.91$ (1) $^\circ$, $V = 1488.1$ \AA^3 , $Z = 4$, $D_x = 1.695$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ \AA , $\mu = 29.8$ cm^{-1} ,

$F(000) = 752$, $T = 293$ K, $R = 0.045$ for 2110 reflections [$I > 2.5\sigma(I)$]. (II) $C_{20}H_{18}BrClN_4S$, $M_r = 461.8$, monoclinic, $P2_1/c$, $a = 8.140$ (1), $b = 14.982$ (7), $c = 16.095$ (9) \AA , $\beta = 99.09$ (3) $^\circ$, $V = 1938.2$ \AA^3 , $Z = 4$, $D_x = 1.583$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ \AA , $\mu = 23.0$ cm^{-1} , $F(000) = 936$, $T = 293$ K, $R = 0.028$ for 2544 reflections [$I > 2.5\sigma(I)$]. The angle between the

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.