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3-(4-Carbamoylphenyl)-1-methyltriazene 1-Oxide

By Reiko Kuroda*†

Cancer Research Campaign Biomolecular Structure Research Group, Department of Biophysics, King's College, 26–29 Drury Lane, London WC2B 5RL, England

and Derry E. V. Wilman

Drug Development Section, Institute of Cancer Research, Clifton Avenue, Sutton, Surrey SM2 5PX, England

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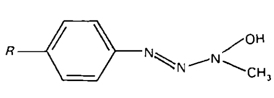
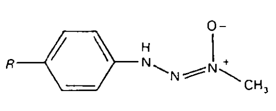
Abstract. $C_8H_{10}N_4O_2$, $M_r = 194{\cdot}19$, $P2_1/a$, $a = 9{\cdot}708\,(2)$, $b = 6{\cdot}7806\,(5)$, $c = 14{\cdot}707\,(2)$ Å, $\beta = 101{\cdot}30\,(1)°$, $V = 949{\cdot}3\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}359$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 8{\cdot}137$ cm^{-1}, $F(000) = 408$, $T = 298$ K, $R = 0{\cdot}037$ for 1028 unique significant reflections. The molecule adopts the *N*-oxide rather than the *N*-hydroxyl form in agreement with the spectroscopic evidence. The atoms of the triazene *N*-oxide group are planar with the oxygen atom *cis* to N(1) of triazene. The atoms of the amide group are also planar. The amide hydrogen atoms are involved in hydrogen bonding.

Introduction. Aryldialkyltriazenes have generated considerable interest as second-generation analogues of the clinically used anti-tumour agent 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide (Wilman & Farmer, 1985). In establishing the structural requirements for anti-tumour activity of this class of compounds, we investigated 3-(4-carbamoylphenyl)-1-methyltriazene 1-oxide [(I*b*), $R = $ —$CONH_2$: CB10-339 (Connors, Goddard, Merai, Ross & Wilman, 1976)] and showed it to be active against the TLX/5 lymphoma and the AdjPC6/A plasmacytoma (Wilman, 1985). It has also been reported as having immunosuppressive activity (Hess, Stewart, Possanza & Freter, 1974).

Compounds of this type are commonly synthesized by the reaction of an aryldiazonium salt with *N*-methylhydroxylamine, and were originally described as 1-aryl-3-hydroxy-3-methyltriazenes (I*a*). However, infrared (Mitsuhashi, Osamura & Shimamura, 1965) and ^{1}H and ^{13}C NMR data (Giumanini, Lassiani, Nisi, Petric & Stanovnik, 1983) tend to suggest that the structure is better described as a 3-aryl-1-methyltriazene 1-oxide (I*b*). As the structural variation will have a considerable effect on the potential of these compounds for metabolism, a necessary prerequisite for anti-tumour activity, we have been prompted to establish the structure conclusively.



(I*a*)



(I*b*)

Experimental. Colourless elongated crystals obtained from ethanol solution, which proved to be twin crystals possessing common *b* and *c* axes. Data collection and structure determination carried out, initially, with a twin crystal and later with a single crystal obtained from acetone solution. Single crystal employed for data collection had dimensions 0·10 × 0·06 × 0·06 mm.

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* To whom correspondence should be addressed.

† Present address: Cancer Research Campaign Biomolecular Structure Unit, Institute of Cancer Research, Block F, Clifton Avenue, Sutton, Surrey SM2 5PX, England.

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Cell dimensions by least-squares refinement of 25 θ values measured on Enraf–Nonius CAD-4 diffractometer. Intensity measurements with ω–2θ scan mode up to $\theta = 70°$ ($0 \leq h \leq 6$, $0 \leq k \leq 8$, $-17 \leq l \leq 17$), max. scan time 120 s, no significant changes in three intensity-control reflections monitored every 3600 s; 1795 unique reflections, 1028 with $I > 3\sigma(I)$ used for refinement. Structure solved by *MULTAN*82 (Main *et al.*, 1982), full-matrix least-squares refinement on *F*. All hydrogen atoms located in difference Fourier map and refined, anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms, respectively. Final $R = 0{\cdot}037$ [$R = \sum(|F_o| - |F_c|)^2/\sum|F_o|^2$], unit weights, number of variables 168, max. $\Delta/\sigma = 0{\cdot}03$, highest peak in final difference synthesis 0·13 e Å^{-3}. Empirical absorption (Walker & Stuart, 1983) and extinction corrections, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations carried out on a PDP 11/34A with *SDP* package (Frenz, 1981).*

Discussion. The molecular structure is shown in Fig. 1. The structures obtained from the twin and the single crystals are virtually the same (the final *R* value was 0·070 for the twin crystal), with a little better accuracy for the result obtained from the single crystal. Thus, only the results from the single crystal will be discussed. Tables 1 and 2 list atomic parameters and molecular geometry, respectively. The results show that the molecule adopts the *N*-oxide tautomeric form, (I*b*), in agreement with the spectroscopic evidence. The N(2)—N(3) bond is shorter than the N(1)—N(2) bond by 0·069 (3) Å, which is again in agreement with the

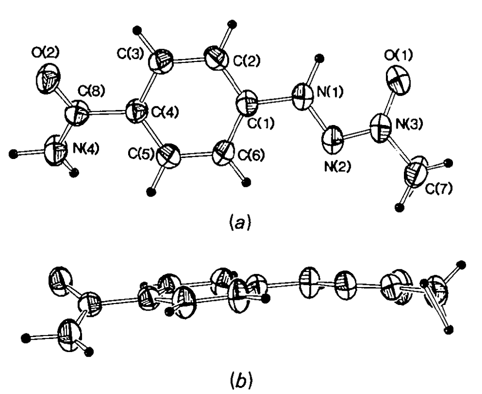

Fig. 1. (*a*) Plan and (*b*) side views of 3-(4-carbamoylphenyl)-1-methyltriazene 1-oxide.

Table 1. *Positional parameters and equivalent isotropic temperature factors*

	x	*y*	*z*	*B*(Å)^2)†
O(1)	0·6931 (2)	0·5859 (3)	0·9888 (1)	4·58 (5)
O(2)	0·6392 (2)	−0·3617 (3)	0·5740 (1)	3·79 (4)
N(1)	0·6504 (2)	0·3561 (3)	0·8532 (2)	3·55 (5)
N(2)	0·5664 (2)	0·5144 (3)	0·8469 (2)	3·45 (5)
N(3)	0·5956 (2)	0·6236 (3)	0·9184 (2)	3·36 (5)
N(4)	0·4074 (2)	−0·3034 (4)	0·5489 (2)	3·94 (5)
C(1)	0·6193 (3)	0·2102 (4)	0·7846 (2)	2·91 (5)
C(2)	0·7088 (3)	0·0510 (4)	0·7900 (2)	3·29 (6)
C(3)	0·6825 (3)	−0·0989 (4)	0·7259 (2)	3·15 (5)
C(4)	0·5634 (2)	−0·0946 (4)	0·6561 (2)	2·73 (5)
C(5)	0·4743 (3)	0·0666 (4)	0·6505 (2)	3·57 (6)
C(6)	0·5024 (3)	0·2198 (4)	0·7134 (2)	3·74 (6)
C(7)	0·5078 (3)	0·7985 (4)	0·9204 (2)	4·41 (7)
C(8)	0·5376 (3)	−0·2629 (4)	0·5895 (2)	2·98 (5)
H(N1)	0·724 (3)	0·330 (5)	0·914 (2)	6·9 (9)*
H(C2)	0·790 (2)	0·044 (4)	0·838 (2)	3·7 (6)*
H(C3)	0·740 (3)	−0·217 (4)	0·729 (2)	5·2 (7)*
H(N41)	0·389 (3)	−0·416 (5)	0·498 (2)	6·4 (8)*
H(N42)	0·339 (3)	−0·239 (4)	0·558 (2)	4·5 (7)*
H(C5)	0·387 (2)	0·070 (4)	0·601 (2)	4·3 (6)*
H(C6)	0·445 (2)	0·334 (4)	0·712 (2)	4·2 (6)*
H(C71)	0·580 (3)	0·903 (5)	0·942 (2)	7·1 (9)*
H(C72)	0·437 (3)	0·773 (5)	0·960 (2)	7·3 (9)*
H(C73)	0·451 (4)	0·826 (6)	0·856 (3)	9 (1)*

* Atoms were refined isotropically.

† Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 2. *Bond lengths* (Å) *and angles* (°)

Numbers in parentheses are e.s.d.'s in the least significant digits.

O(1)—N(3)	1·284 (3)	C(2)—C(3)	1·376 (4)
O(2)—C(8)	1·250 (3)	C(2)—H(C2)	0·95 (2)
N(1)—N(2)	1·340 (3)	C(3)—C(4)	1·388 (3)
N(1)—C(1)	1·403 (3)	C(3)—H(C3)	0·97 (3)
N(1)—H(N1)	1·05 (3)	C(4)—C(5)	1·386 (4)
N(2)—N(3)	1·271 (3)	C(4)—C(8)	1·492 (4)
N(3)—C(7)	1·464 (4)	C(5)—C(6)	1·382 (4)
N(4)—C(8)	1·317 (3)	C(5)—H(C5)	1·01 (2)
N(4)—H(N41)	1·06 (3)	C(6)—H(C6)	0·95 (3)
N(4)—H(N42)	0·83 (3)	C(7)—H(C71)	1·00 (3)
C(1)—C(2)	1·378 (4)	C(7)—H(C72)	1·00 (3)
C(1)—C(6)	1·387 (3)	C(7)—H(C73)	1·01 (3)

N(2)—N(1)—C(1)	118·2 (2)	C(3)—C(4)—C(5)	118·7 (2)
N(2)—N(1)—H(N1)	120 (2)	C(3)—C(4)—C(8)	118·6 (2)
C(1)—N(1)—H(N1)	121 (2)	C(5)—C(4)—C(8)	122·8 (2)
N(1)—N(2)—N(3)	112·1 (2)	C(4)—C(5)—C(6)	121·0 (2)
O(1)—N(3)—N(2)	124·1 (2)	C(4)—C(5)—H(C5)	119 (2)
O(1)—N(3)—C(7)	119·0 (2)	C(6)—C(5)—H(C5)	120 (2)
N(2)—N(3)—C(7)	116·9 (2)	C(1)—C(6)—C(5)	119·7 (2)
C(8)—N(4)—H(N41)	119 (2)	C(1)—C(6)—H(C6)	116 (1)
C(8)—N(4)—H(N42)	123 (2)	C(5)—C(6)—H(C6)	124 (1)
H(N41)—N(4)—H(N42)	118 (2)	N(3)—C(7)—H(C71)	102 (2)
N(1)—C(1)—C(2)	117·7 (2)	N(3)—C(7)—H(C72)	110 (2)
N(1)—C(1)—C(6)	122·6 (2)	N(3)—C(7)—H(C73)	110 (2)
C(2)—C(1)—C(6)	119·6 (2)	H(C71)—C(7)—H(C72)	117 (3)
C(1)—C(2)—C(3)	120·5 (2)	H(C71)—C(7)—H(C73)	113 (3)
C(1)—C(2)—H(C2)	120 (2)	H(C72)—C(7)—H(C73)	105 (3)
C(3)—C(2)—H(C2)	119 (2)	O(2)—C(8)—N(4)	121·8 (2)
C(2)—C(3)—C(4)	120·5 (2)	O(2)—C(8)—C(4)	119·5 (2)
C(2)—C(3)—H(C3)	123 (2)	N(4)—C(8)—C(4)	118·7 (2)
C(4)—C(3)—H(C3)	116 (2)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42366 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tautomer (I*b*). The four atoms of the triazene *N*-oxide group are closely planar ($\chi^2 = 4$). The average plane of the group forms a dihedral angle of 11 (1)° with the phenyl ring. This is probably due to repulsion between H(C2) and H(N1) atoms [H(C2)···H(N1) = 2·39 Å, C(2)—C(1)—N(1)—N(2) = 172·3 (4)°, C(2)—C(1)—N(1)—H(N1) = −13·6 (4)°]. N(1) and N(2) atoms do not deviate significantly from the phenyl ring [−0·056 (2) and −0·020 (2) Å, respectively], hence the delocalization is extended to these atoms, resulting in the short C(1)—N(1) distance of 1·403 (3) Å. The N(1) and O(1) atoms are *cis* to each other.

The four atoms of the amide group are highly planar ($\chi^2 = 0$), and the group is inclined at an angle of 27 (1)° to the average plane of the phenyl group. This probably results from steric hindrance between N(4) and C(5) and between the O(2) and C(3) atoms. The H(N42)···H(C5) distance is 2·21 (4) Å, which would be 2·02 Å if the two groups were coplanar.

Both of the amide hydrogen atoms participate in hydrogen bonding. H(N41) forms a bond to the O(2) atom of the neighbouring molecule related by an inversion centre, while H(N42) links an *a*-glide-plane-related molecule *via* O(2) [H(N41)···O(2) = 1·83 (4) Å, O(2)···H(N41)—N(4) = 170 (4)°; H(N42)···O(2) = 2·11 (5) Å, O(2)···H(N42)—N(4) = 166 (4)°].

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Trichloro(2-phenylthiophenyl)tellurium

BY R. CHAKRAVORTY,[*] K. J. IRGOLIC AND EDWARD A. MEYERS[†]

Department of Chemistry, Texas A&M University, College Station, Texas 77843, *USA*

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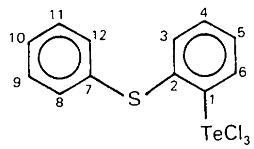
Abstract. $[\mathrm{Te(C_{12}H_9S)Cl_3}]$, $M_r = 419{\cdot}2$, monoclinic, $P2_1/c$, $a = 9{\cdot}428$ (2), $b = 11{\cdot}878$ (1), $c = 13{\cdot}095$ (2) Å, $\beta = 96{\cdot}57$ (1)°, $V = 1456{\cdot}8$ Å^3, $D_x = 1{\cdot}91$ Mg m^{-3}, $Z = 4$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}77$ mm^{-1}, $F(000) = 800$, $T = 296$ K, $R = 0{\cdot}033$ for 2283 reflections with $I > 0{\cdot}5\sigma(I)$. In $\mathrm{C_6H_5{-}S{-}C_6H_4{-}TeCl_3}$ the phenyl rings and C—Te and C—S bonds are normal, as is the T-shaped $\mathrm{TeCl_3}$ group. There is a close contact between the *ortho* substituents Te and S.

Introduction. It was of interest to determine the structure of the title compound in order to (1) establish the coordination around Te and (2) find out how the Group VI *ortho* substituents, S and Te, affect each other and the remainder of the structure.



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[*] On leave from the Department of Chemistry, Rammohan College, Calcutta, India.

[†] Author to whom all correspondence should be addressed.

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