Crystal and Molecular Structure of 3-Methyl-1-*p*-tolyltriazene †

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Crystals of the title compound have monoclinic symmetry with $a = 8.196(1)$, $b = 8.545(2)$, $c = 13.163(2)$ Å, $\beta = 112.72(2)°$, and space group $P2_1/c$. For 1 088 observed independent reflections collected on a four-circle diffractometer the R-factor reached 0.063 after full-matrix least-squares refinement. The triazene unit has a double bond between N(1) and N(2) with a hydrogen atom and a methyl group both carried by N(3). A 21—22° twist about the bond joining ring to triazene helps to relieve steric hindrance. Molecules are linked by N–H ··· N hydrogen bonding. The preference for the tautomeric form p-$CH_3{\cdot}C_6H_4{\cdot}N{=}N{-}NH{-}CH_3$ in the solid state is consistent with the behaviour in solution, as determined by n.m.r. spectroscopy.

A wide variety of triazenes show anti-tumour activity and one such compound, 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide (DTIC, NSC 45388) is in clinical use for the treatment of human malignant melanoma.[1] The 3,3-dimethyltriazenes are postulated to undergo metabolic conversion into monomethyltriazenes and a detailed study by Connors *et al.*[2] suggests that only those dialkyltriazenes which can be metabolised to monomethyltriazenes have anti-tumour activity *in vivo*. More recent work by Gescher *et al.*[3] has shown that metabolism of dimethyltriazenes generates a mixture of selective and non-selective metabolites and that the monomethyltriazenes appear to be non-selective.

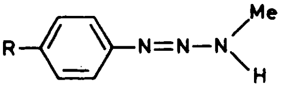
1-Aryl-3-methyltriazenes may exist in either of two tautomeric forms (1) and (2). This tautomerism has been extensively studied by spectroscopic techniques, in particular by n.m.r. spectroscopy,[4,5] which clearly shows that electron-withdrawing substituents in the aryl group favour the ' unconjugated ' tautomer (2). The work reported here involves a crystal-structure determination for 3-methyl-1-*p*-tolyltriazene (MTT), undertaken in order to verify the predicted preference for tautomer (1) (R = Me) and to compare its molecular geometry with that of some 1-aryl-3,3-dimethyltriazenes.[6,7]

Experimental

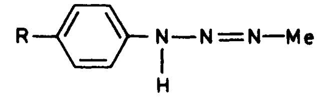
The title compound formed needle crystals from ethanol. A specimen 0.16 × 0.32 × 1.2 mm was selected for crystallographic analysis. Data were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å.

Crystal Data.—3-Methyl-1-*p*-tolyltriazene, $C_8H_{11}N_3$, $M = 149.20$. Monoclinic, $a = 8.196(1)$, $b = 8.545(2)$, $c = 13.163(2)$ Å, $\beta = 112.72(2)$, $U = 850.3$ Å^3, $Z = 4$, $D_m = 1.17(1)$, $D_c = 1.165$ g cm^{-3}, $F(000) = 320$, space group $P2_1/c$ uniquely determined.

Structural Analysis.—Intensity data were collected by the $\omega - 2\theta$ scan technique. Measurements were corrected for Lorentz-polarization effects but not for absorption since $\mu = 0.43$ cm^{-1} for Mo-K_α radiation. Two standard reflections were monitored for orientation and intensity. A linear correction to intensity *versus* time was derived from their decline and this was universally applied. The 1 627 reflections collected in the range $2° \leqslant \theta \leqslant 25°$ were merged to give 1 483 independent reflections, of which 1 088 were deemed observed ($F > 3\sigma$) and used in refinement.



(1)



(2)

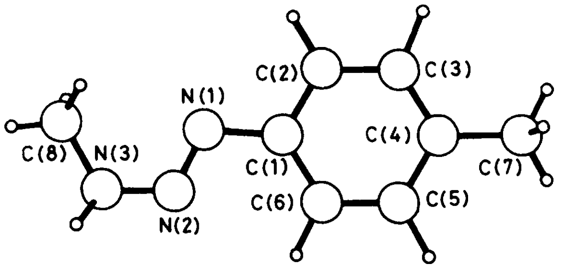


Figure 1. PLUTO[9] drawing of the molecule projected on to its least-squares plane

The structure was determined by the EEES direct methods procedure in SHELX.[8] All non-hydrogen atoms appeared in the E-map. They were treated as carbon and subjected to least-squares refinement of positions and isotropic temperature factors. The nitrogen atoms were distinguished from carbon by their lower isotropic temperature factors and shorter bond distances and were designated as such. Hydrogen positions were established from a difference electron density map and not refined. One common isotropic temperature factor was refined for the methyl hydrogen atoms plus 3-H, and another one was refined for all remaining hydrogen atoms. In the final refinement cycles positional parameters and anisotropic thermal parameters for non-hydrogen atoms were refined along with an empirical extinction correction and those hydrogen parameters detailed above. Refinement was based on F magnitudes weighted by $w = 1/[\sigma^2(F_o) + gF_o^2]$, where g converged to 0.0058. The final discrepancy indices were $R = 0.063$ and $R_g = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.108$. No feature on a final difference electron density map exceeded ± 0.25 e Å^{-3}. In particular, there was no credible peak near triazine N(1) which could suggest a type-(2) tautomer. The molecule and its numbering scheme are presented in Figure 1; co-ordinates and non-hydrogen equivalent isotropic temperature factors are listed in Table 1. Observed and calculated

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Table 1. Atom positional parameters (fractional co-ordinates × 10^4; × 10^3 for hydrogen atoms) and equivalent isotropic temperature factors (× 10^4) with standard deviations in parentheses

Atom	x	y	z	U_{iso} (Å^2)
C(1)	7 634(3)	2 119(3)	1 710(2)	444(9)
C(2)	8 937(3)	3 253(3)	2 128(2)	533(9)
C(3)	10 152(4)	3 514(3)	1 652(2)	585(10)
C(4)	10 102(3)	2 681(3)	740(2)	534(10)
C(5)	8 761(4)	1 572(3)	305(2)	570(10)
C(6)	7 550(4)	1 287(3)	777(2)	547(9)
C(7)	11 435(4)	2 981(4)	228(3)	744(14)
C(8)	4 434(5)	1 330(4)	3 395(3)	763(15)
N(1)	6 457(3)	1 921(2)	2 260(2)	495(8)
N(2)	5 701(3)	587(2)	2 064(2)	535(8)
N(3)	4 592(3)	321(3)	2 551(2)	593(9)
H(2)	899	395	282	
H(3)	1 102	456	203	
H(5)	864	92	−45	
H(6)	653	44	43	
H(7A)	1 176	419	23	
H(7B)	1 261	258	60	
H(7C)	1 132	245	−40	
H(8A)	378	86	379	
H(8B)	573	147	397	
H(8C)	403	220	314	
H(31)	457	−95	281	

structure factors, anisotropic thermal parameters, hydrogen atom geometry, and least-squares planes are given in Supplementary Publication No. SUP 23755 (11 pp).*

Results and Discussion

Bond lengths, bond angles, and selected torsion angles are given in Tables 2, 3, and 4 respectively. This structure (MTT) forms part of a series of phenyltriazene structures differing in the degree of substitution at N(3); it may be compared with 2-(3,3-dimethyl-1-triazeno)phenyl-1-carboxamide (DTPC)[6] and 1-(*p*-ethoxycarbonylphenyl)-3-methyl-3-hydroxymethyltriazene (HMT).[7] The geometry of the triazene chain differs only slightly in all three structures despite the variations in the substituent groups. The bond linking the ring to the triazene moiety, C(1)–N(1), is 1.422(3) Å long in MTT, 1.429(8) Å in DTPC, and 1.423(5) Å in HMT; for N(1)–N(2) the distances are 1.275(3), 1.281(7), and 1.280(7) Å, respectively, and for N(2)–N(3) they are 1.319(3), 1.309(7), and 1.319(6) Å. The presence of a type-(1) tautomer in MTT is confirmed once again. Even the N(3)–C distances, which should be most sensitive to the steric and inductive effects of an extra substituent, are similar in the three structures: 1.451(4) Å in MTT, 1.45(1) and 1.46(1) Å in DTPC, and 1.467(7) and 1.452(7) Å in HMT.

The bond angles at N(3) and N(1) in the three molecules do not differ by more than 0.8°, but the N(1)–N(2)–N(3) angle is larger in MTT [115.4(2)°] than in DTPC [113.3(5)°] or in HMT [113.6(3)°]. In all three molecules the steric hindrance between N(2) and the ring is reduced by opening the relevant C–C(1)–N(1) angle above 120°, to 125.0(2)° in MTT and 125.7(3)° in HMT, but only to 121.3(6)° in DTPC where N(1) accepts a hydrogen-bonded proton from an *ortho*-substituent.

Relief of N(2)–ring interference is also achieved by twisting the C(1)–N(1) bond. In MTT the twist is 21—22°. The N(1)–N(2) double bond is almost free of twisting, but N(2)–N(3) does sustain a −10.0(5)° twist as measured by the N(1)–N(2)–N(3)–C(8) torsion angle. The rest of the molecule is held largely coplanar as is consistent with a highly conjugated system. It was suggested that the planarity of the DTPC molecule[6] results from the combined effects of conjugation and intramolecular hydrogen bonding. However, the evidence from MTT is that the requirements of conjugation can alone impose a considerable degree of planarity.

Table 2. Bond distances for C and N atoms with standard deviations in parentheses

Bond	Distance (Å)
C(1)–C(6)	1.398(4)
C(1)–C(2)	1.389(4)
C(2)–C(3)	1.384(4)
C(3)–C(4)	1.383(4)
C(4)–C(5)	1.396(4)
C(5)–C(6)	1.381(4)
C(4)–C(7)	1.511(4)
C(1)–N(1)	1.422(3)
N(1)–N(2)	1.275(3)
N(2)–N(3)	1.319(3)
N(3)–C(8)	1.451(4)

Table 3. Bond angles for C and N atoms with standard deviations in parentheses

Bond	Angle (°)
C(6)–C(1)–C(2)	118.2(2)
C(2)–C(1)–N(1)	116.8(2)
C(6)–C(1)–N(1)	125.0(2)
C(1)–C(2)–C(3)	120.7(2)
C(2)–C(3)–C(4)	121.7(2)
C(3)–C(4)–C(5)	117.4(2)
C(3)–C(4)–C(7)	121.1(2)
C(5)–C(4)–C(7)	121.5(2)
C(4)–C(5)–C(6)	121.6(2)
C(1)–C(6)–C(5)	120.4(2)
C(1)–N(1)–N(2)	112.1(2)
N(1)–N(2)–N(3)	115.4(2)
N(2)–N(3)–C(8)	123.5(2)

Table 4. Selected torsion angles. Estimated standard deviations are *ca.* 0.5°

Bonds	Torsion angle (°)
C(1)–C(2)–C(3)–C(4)	1.0
C(2)–C(3)–C(4)–C(5)	0.7
C(2)–C(3)–C(4)–C(7)	179.9
C(3)–C(4)–C(5)–C(6)	−1.4
C(7)–C(4)–C(5)–C(6)	179.5
C(4)–C(5)–C(6)–C(1)	−0.3
C(2)–C(1)–C(6)–C(5)	1.4
N(1)–C(1)–C(6)–C(5)	179.9
C(6)–C(1)–C(2)–C(3)	−2.0
N(1)–C(1)–C(2)–C(3)	179.3
C(2)–C(1)–N(1)–N(2)	−159.3
C(6)–C(1)–N(1)–N(2)	22.1
C(1)–N(1)–N(2)–N(3)	179.8
N(1)–N(2)–N(3)–C(8)	−10.0

Molecules in the unit cell (Figure 2), related by a screw axis, are linked by N(1)–H · · · N(3) hydrogen bonds at an N · · · N distance of 3.067(3) Å and an N–H · · · N angle of 156°. The molecules associate into aromatic and nitrogenous domains.

This study has demonstrated unequivocally that the monomethyltriazene (MTT) exists in the solid state exclusively as the conjugated tautomer (1). This result may be compared with

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* For details of the Supplementary Publication Scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

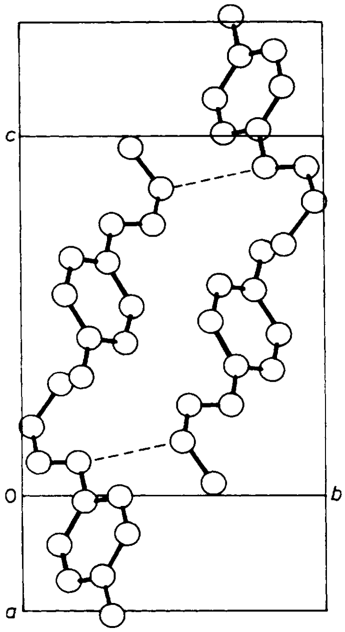

Figure 2. PLUTO[9] drawing of the unit cell contents viewed down the a^* axis. The N–H · · · N hydrogen bond is shown as a dashed line

the studies of this compound[4] and other 3-alkyl-1-*p*-tolyltriazenes[5] in solution; n.m.r. evidence shows that tautomer (1) is predominant in concentrated solution and resolution of ^{1}H signals owing to the minor tautomer (2) is only possible in dilute solutions.[4] If the solid state may be regarded as the ultimate extrapolation of an increasingly concentrated solution, then the conclusion of this crystal-structure determination is entirely consistent with the behaviour in solution.

Acknowledgements

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