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## Synthesis and Structure of 3-(4-Carbamoylphenyl)-1,3-dimethyltriazene 1-Oxide

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**Abstract.** C<sub>9</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>, *M<sub>r</sub>* = 208.22, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.345 (1), *b* = 5.059 (1), *c* = 21.531 (2) Å, β = 95.24 (1)°, *V* = 1013.6 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.364 g cm<sup>-3</sup>, λ(Cu *Kα*) = 1.5418 Å, μ(Cu *Kα*) = 7.955 cm<sup>-1</sup>, *F*(000) = 440, *T* = 298 K, *R* = 0.063 for 1112 significant reflections. The analysis confirms the *N*-oxide character of this compound. The triazene system is non-coplanar with the phenyl group, as a result of the relief of steric hindrance caused by the methyl group at N(1).

**Introduction.** Aryldialkyltriazenes have been examined extensively for possible antitumour activity in a continuing search for second-generation analogues of 5-(3,3-dimethyl-1-triazenyl)-1*H*-imidazole-4-carboxamide (DTIC; Wilman & Farmer, 1986). As a part of this study we have investigated different types of triazene *N*-oxide, including the title compound (I), in relation to both their structure and their antitumour activity (Wilman, 1985). The recent X-ray crystallographic analysis of 3-(4-carbamoylphenyl)-1-methyltriazene 1-oxide (II) (Kuroda & Wilman, 1985) has shown that, at least in the solid state, the *N*-oxide form is preferred to the *N*-hydroxyl.

The present study examines the geometry of the triazene analogue where *N*-methylation of (II) has

forced the *N*-oxygenated substituent into the *N*-oxide form, since there is no longer a proton directly attached to an N atom (which instead now carries the methyl group).

**Experimental.** Compound (II) (Connors, Goddard, Merai, Ross & Wilman, 1976) was reacted successively in dimethylformamide with sodium hydride and iodomethane by the method of Miesel (1976) to give the title compound (CB 10-439) following chromatography on silica gel (Merck 7734) with ethyl acetate as eluant and crystallization from benzene; m.p. 478–480 K, 40% yield. Analysis calculated for C<sub>9</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>: C, 51.9; H, 5.8; N, 26.9%. Found: C, 52.0; H, 5.9; N, 27.4%.

Colourless elongated crystals were readily obtained from ethanolic solution, although their tendency to twin caused difficulties in the selection of suitable single crystals. A crystal used for data collection had dimensions 0.04 × 0.05 × 0.04 mm. Cell dimensions from least-squares refinement of 25 θ values measured on an Enraf–Nonius CAD-4 diffractometer. Intensity measurements with ω–2θ scans, 1.5 < θ < 65.0°. 0 ≤ *h* ≤ 10, 0 ≤ *k* ≤ 5, –25 ≤ *l* ≤ 25, max. scan time 90 s. No significant change in three control reflections measured every 3600 s. 1881 unique reflections were measured, of which 1112 had *I* > 2σ(*I*) and were used for refinement. Structure solved by *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refined by a full-matrix

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least-squares procedure on  $F$ . Some H-atom positions located in difference Fourier map, others generated by standard geometric considerations. Nonhydrogen-atom positional and anisotropic thermal parameters refined, together with the majority of H-atom positional and isotropic thermal parameters. Hydrogen atoms H(4A), H(4B) were kept fixed as they would not refine satisfactorily. Function minimized was  $\sum w(F_o - F_c)^2$ ,  $w$  defined as  $[\sigma^2(F_o) + 0.04(F_o)^2]^{-1}$ . ( $F_o$  derived from counting statistics.  $R = 0.063$ ,  $wR = 0.060$ , max. (shift/e.s.d.) = 0.02, number of variables 184,  $\rho_{\max} 0.22$ ,  $\rho_{\min} -0.31 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). No corrections for absorption or secondary extinction. Calculations carried out with the *SDP* package (Frenz, 1981) on a VAX 11/750 computer. Atomic positional parameters and  $U_{\text{eq}}$  values are given in Table 1.\*

**Discussion.** The molecular structure of (I) is shown in Fig. 1, and bond distances and angles are given in Table 2.

The pattern of non-equal N—N bond lengths observed for (I) is in accord with that found for (II) (Kuroda & Wilman, 1985). Thus, the N(1)—N(2) distances of 1.383 (2) and 1.340 (3) Å respectively are indicative of greater double-bond character in the N(2)—N(3) bonds. These are of length 1.280 (2) (I) and 1.271 (3) Å (II). In the latter structure, this may be taken as good evidence for the major tautomer being the N(3) oxide, with a proton on N(1), rather than the N(3) hydroxide with N(1)—N(2) having formal double-bond character, in accord with spectroscopic data (Guimanini, Lassiani, Nisi, Petric & Stanovnik, 1983). In the case of (I) the existence of a methyl substituent on N(1) excludes such a tautomerism. Thus O(1)—N(3)

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43517 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

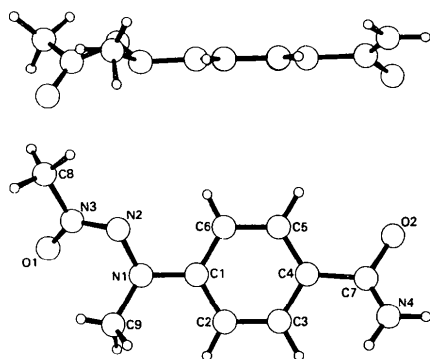


Fig. 1. Two computer-drawn orthogonal views of the molecular structure of the title compound.

Table 1. Atomic positions and isotropic or equivalent isotropic temperature factors

|       | x          | y          | z          | $B(\text{\AA}^2)$ |
|-------|------------|------------|------------|-------------------|
| O(1)  | 0.5070 (3) | 0.3064 (7) | 0.4377 (1) | 3.94 (7)          |
| O(2)  | 0.0106 (4) | 0.2746 (8) | 0.0725 (2) | 5.45 (9)          |
| N(1)  | 0.3689 (4) | 0.5043 (8) | 0.3388 (2) | 3.08 (8)          |
| N(2)  | 0.2909 (4) | 0.4011 (9) | 0.3847 (2) | 3.55 (9)          |
| N(3)  | 0.3718 (4) | 0.3127 (9) | 0.4313 (2) | 3.43 (8)          |
| N(4)  | 0.0738 (4) | 0.7021 (7) | 0.0636 (1) | 2.32 (6)          |
| C(1)  | 0.2919 (5) | 0.505 (1)  | 0.2796 (2) | 2.66 (9)          |
| C(2)  | 0.3296 (5) | 0.678 (1)  | 0.2334 (2) | 3.2 (1)           |
| C(3)  | 0.2569 (5) | 0.6718 (9) | 0.1746 (2) | 2.99 (9)          |
| C(4)  | 0.1476 (5) | 0.4897 (9) | 0.1595 (2) | 2.56 (9)          |
| C(5)  | 0.1114 (5) | 0.317 (1)  | 0.2055 (2) | 2.94 (9)          |
| C(6)  | 0.1823 (5) | 0.323 (1)  | 0.2645 (2) | 2.93 (9)          |
| C(7)  | 0.0746 (4) | 0.504 (1)  | 0.0945 (2) | 2.83 (9)          |
| C(8)  | 0.2946 (6) | 0.217 (1)  | 0.4834 (2) | 5.5 (1)           |
| C(9)  | 0.4623 (6) | 0.732 (1)  | 0.3567 (2) | 5.0 (1)           |
| H(2)  | 0.406 (4)  | 0.805 (9)  | 0.242 (2)  | 4 (1)*            |
| H(3)  | 0.283 (5)  | 0.80 (1)   | 0.143 (2)  | 5 (1)*            |
| H(5)  | 0.970 (4)  | 0.687 (9)  | 0.305 (2)  | 4 (1)*            |
| H(6)  | 0.845 (4)  | 0.700 (9)  | 0.207 (2)  | 3.0 (9)*          |
| H(8C) | 0.190 (4)  | 0.216 (9)  | 0.469 (2)  | 4 (1)*            |
| H(8B) | 0.312 (6)  | 0.15 (1)   | -0.981 (2) | 7 (2)*            |
| H(8A) | 0.324 (6)  | 0.47 (1)   | -0.004 (3) | 8 (2)*            |
| H(9C) | 0.556 (8)  | 0.71 (2)   | 0.334 (3)  | 12 (2)*           |
| H(9A) | 0.577 (7)  | 0.40 (1)   | 0.156 (3)  | 9 (2)*            |
| H(9B) | 0.492 (6)  | 0.72 (1)   | 0.394 (3)  | 9 (2)*            |
| H(4A) | 0.1185     | 0.8556     | 0.0802     | 5*                |
| H(4B) | 0.0257     | 0.7003     | 0.0227     | 5*                |

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

Table 2. Bond distances (Å) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

|                  |           |                  |           |
|------------------|-----------|------------------|-----------|
| O(1)—N(3)        | 1.259 (2) | C(3)—C(4)        | 1.392 (3) |
| O(2)—C(7)        | 1.368 (2) | C(3)—H(3)        | 0.98 (2)  |
| N(1)—N(2)        | 1.383 (2) | C(4)—C(5)        | 1.387 (3) |
| N(1)—C(1)        | 1.405 (2) | C(4)—C(7)        | 1.500 (2) |
| N(1)—C(9)        | 1.473 (3) | C(5)—C(6)        | 1.379 (2) |
| N(2)—N(3)        | 1.280 (2) | C(5)—H(5)        | 1.02 (2)  |
| N(3)—C(8)        | 1.470 (3) | C(6)—H(6)        | 0.93 (2)  |
| N(4)—C(7)        | 1.205 (2) | C(8)—H(8C)       | 1.00 (2)  |
| N(4)—H(4A)       | 0.938 (1) | C(8)—H(8B)       | 1.01 (3)  |
| N(4)—H(4B)       | 0.950 (1) | C(8)—H(8A)       | 1.03 (3)  |
| C(1)—C(2)        | 1.396 (3) | C(9)—H(9C)       | 1.05 (4)  |
| C(1)—C(6)        | 1.393 (3) | C(9)—H(9A)       | 0.98 (3)  |
| C(2)—C(3)        | 1.381 (3) | C(9)—H(9B)       | 0.84 (3)  |
| C(2)—H(2)        | 0.96 (2)  |                  |           |
| N(2)—N(1)—C(1)   | 112.9 (2) | C(4)—C(5)—C(6)   | 121.0 (2) |
| N(2)—N(1)—C(9)   | 116.5 (2) | C(4)—C(5)—H(5)   | 118. (1)  |
| C(1)—N(1)—C(9)   | 118.5 (2) | C(6)—C(5)—H(5)   | 121. (1)  |
| N(1)—N(2)—N(3)   | 112.3 (2) | C(1)—C(6)—C(5)   | 120.8 (2) |
| O(1)—N(3)—N(2)   | 127.6 (2) | C(1)—C(6)—H(6)   | 122. (1)  |
| O(1)—N(3)—C(8)   | 117.8 (2) | C(5)—C(6)—H(6)   | 117. (1)  |
| N(2)—N(3)—C(8)   | 114.6 (2) | O(2)—C(7)—N(4)   | 122.2 (2) |
| C(7)—N(4)—H(4A)  | 119.9 (2) | O(2)—O(7)—C(4)   | 115.5 (2) |
| C(7)—N(4)—H(4B)  | 118.9 (2) | O(2)—C(7)—C(4)   | 122.2 (2) |
| H(4A)—N(4)—H(4B) | 121.3 (2) | N(3)—C(8)—H(8C)  | 107. (1)  |
| N(1)—C(1)—C(2)   | 120.4 (2) | N(3)—C(8)—H(8B)  | 108. (2)  |
| N(1)—C(1)—C(6)   | 121.0 (2) | N(3)—C(8)—H(8A)  | 111. (2)  |
| C(2)—C(1)—C(6)   | 118.5 (2) | H(8C)—C(8)—H(8B) | 109. (2)  |
| C(1)—C(2)—C(3)   | 120.2 (2) | H(8C)—C(8)—H(8A) | 108. (2)  |
| C(1)—C(2)—H(2)   | 120. (1)  | H(8B)—C(8)—H(8A) | 113. (2)  |
| C(3)—C(2)—H(2)   | 119. (1)  | N(1)—C(9)—H(9C)  | 108. (2)  |
| C(2)—C(3)—C(4)   | 121.3 (2) | N(1)—C(9)—H(9A)  | 115. (2)  |
| C(2)—C(3)—H(3)   | 118. (1)  | N(1)—C(9)—H(9B)  | 108. (2)  |
| C(4)—C(3)—H(3)   | 120. (1)  | H(9C)—C(9)—H(9A) | 105. (3)  |
| C(3)—C(4)—C(5)   | 118.2 (2) | H(9C)—C(9)—H(9B) | 103. (3)  |
| C(3)—C(4)—C(7)   | 116.6 (2) | H(9A)—C(9)—H(9B) | 116. (3)  |
| C(5)—C(4)—C(7)   | 125.1 (2) |                  |           |

would be expected to show true *N*-carbonyl character; this is indeed the case as its bond length is 0.025 Å shorter than in (II). The similarly somewhat shortened N(1)–N(2) bond in (I) is not observed. This is presumably on account of the loss of in-plane delocalization with the aryl group (see below).

The carboxamide group at C(4) in (I) is closely coplanar, with the five-atom group O(2), C(7), N(4), H(4A), H(4B) having a  $\chi^2$  of 2. This plane is inclined at 25.0 (5)° to the phenyl group, and compares well with the 27° value found in (II). In both cases the deviation from coplanarity can best be ascribed to the relief of otherwise close contacts between hydrogen atoms on the phenyl ring and –N(4)H<sub>2</sub> group.

The triazene oxide system [N(1), N(2), N(3), O(1)] is closely coplanar ( $\chi^2 = 7$ ), as found in (II). The O(1) atom and the methyl group on N(1) are in a *cis* configuration. However, in contrast to (II), this N(1) substituent is markedly out of the triazene plane [C(9) is out of the four-atom plane by 1.175 (5) Å] and the N(2)–N(3)–O(1) angle is distorted. The triazene plane itself is at an angle of 42.3 (5)° with the phenyl ring, compared to 11° in (II). These out-of-plane distortions are probably due to the relief of steric hindrances arising from the methyl group at N(1). These factors

result in the title compound having a significantly different bonding geometry for the triazene moiety from (II).

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## Structure of the 2:1 Complex of Phenol and Urea

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**Abstract.** (NH<sub>2</sub>)<sub>2</sub>CO.2C<sub>6</sub>H<sub>5</sub>OH, *M<sub>r</sub>* = 248.3, monoclinic, *Cc*, *a* = 26.933 (4), *b* = 6.646 (3), *c* = 7.428 (3) Å,  $\beta$  = 92.38 (3)°, *V* = 1328 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.23, *D<sub>x</sub>* = 1.24 g cm<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71069 Å,  $\mu$  = 0.83 cm<sup>-1</sup>, *F*(000) = 528, *T* = 293 K, *R* = 0.053 for 562 unique observed [*I*/σ(*I*) ≥ 2.0] reflections. The two phenol molecules are linked by hydrogen bonds [O...O 2.61 (1) and 2.70 (1) Å] to the carbonyl oxygen of the urea. The urea is further linked to two separate phenol molecules by NH...O hydrogen bonds [N...O 2.95 (1) and 3.05 (1) Å], forming infinite chains. NH...O hydrogen bonds [N...O 3.08 (1) Å] link these chains into stacks along *c*. There is no hydrogen bonding between stacks.

**Introduction.** Phase equilibrium studies of the phenol–urea system by thermal analysis reveal the existence of a compound having 2:1 stoichiometry (Philip, 1903; Puschin & Konig, 1928; Palobekov & Bergman, 1966). Evidence has been adduced from IR spectra for the participation of all of the N and O atoms in hydrogen bonding (Chesnokov & Bokhovkin, 1966). We have determined the crystal structure of the complex in order to ascertain conclusively the nature of the bonding between the constituent molecules.

**Experimental.** The compound was obtained by melting together a mixture of phenol and urea (66 mol% phenol and 33 mol% urea). Very thin plates developed on