

Atomic parameters are given in Table 1 and bond distances and angles in Table 2.\*

**Discussion.** The structure consists of cations and chloride ions held together by two weak hydrogen bonds (N—H...Cl) of 3.15 Å. The absolute configuration is confirmed as *S*. The backbone of the molecule is almost fully extended (Fig. 1 and Table 3) and the maximum deviation from perfect staggering is 17°. The phenyl ring [C(41)] can be seen to be nearly perpendicular to the chain. This structure will be used as a reference for determining the absolute configuration and conformations of pharmacologically active molecules containing a 1-methyl-3-phenylpropylamine moiety and in particular that of the four

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36227 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

enantiomers present in the antihypertensive drug, labetalol [Trandate®] (Brittain, Drew & Levy, 1981).

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## Tetramethylenefurazan *N*-Oxide at 125 K

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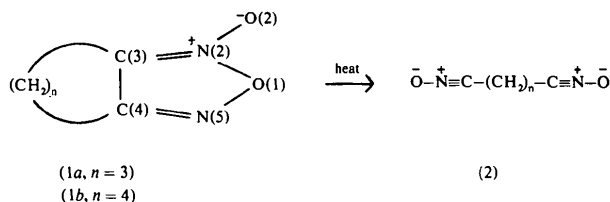
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**Abstract.** C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 140.1, orthorhombic, *Pbca*. At 125 K: *a* = 9.54, *b* = 12.61, *c* = 10.69 Å (e.s.d.'s 0.3% assumed), *U* = 1286.0 Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.45 Mg m<sup>-3</sup>, Cu *K*α radiation (Ni filter), λ = 1.5418 Å, μ(Cu *K*α) = 0.889 mm<sup>-1</sup>. A partially disordered structure has been refined to *R* = 4.2% using 800 photographic (microdensitometer) intensities. A recent X-ray structure analysis of trimethylenefurazan *N*-oxide [Barnes, Barrow, Harding, Paton, Ashcroft, Crosby & Joyce (1979). *J. Chem. Res. (S)*, pp. 314–315] revealed angle strain in the five-membered carbocyclic ring and an unusually long O(1)–N(2) bond, 1.494 (3) Å, in the furazan ring. The structure of the title compound shows that addition of a further methylene group alleviates the angle strain in the carbocycle and the O(1)–N(2) bond shortens to 1.465 (4) Å.

**Introduction.** Trimethylenefurazan *N*-oxide (1*a*), which had hitherto been believed unstable, has recently been synthesized and its molecular geometry established by X-ray crystallography (Barnes *et al.*, 1979). The main

structural features of (1*a*) are an unusually long O(1)–N(2) bond, 1.494 (3) Å, and angle strain in the five-membered carbocyclic ring. The O(1)–N(2) distance implies an incipient weakening of this bond and might be related with the observation of thermal decomposition to the bis(nitrile oxide) (2), though the thermolytic ring fission of (1*a*) is not unusually facile (Barnes *et al.*, 1979). The next member in the series, tetramethylenefurazan *N*-oxide, (1*b*), is markedly more resistant to thermal decomposition (Paton, 1981) and was investigated by X-ray crystallography to determine the structural consequences of increasing the size of the carbocyclic ring.



A sample of tetramethylenefurazan *N*-oxide (m.p. 317–318 K), prepared by the method of Boyer & Toggweiler (1957), was kindly provided by Drs J. F. Barnes and R. M. Paton. Colourless, distorted-octahedral crystals were obtained by recrystallization from 40/60 petroleum ether. The crystals sublime rapidly at room temperature. X-ray photographs of crystals maintained at 125 K were exposed using a Nonius Weissenberg goniometer fitted with a Nonius nitrogen-gas-stream low-temperature attachment. Three different crystals were used to record reflexions by the multiple-film-pack equi-inclination Weissenberg method as follows: crystal (1),  $h0-4l$ ; crystal (2),  $hk0$ ; crystal (3),  $0-5kl$ . Each crystal had approximate dimensions  $0.6 \times 0.6 \times 0.5$  mm. Intensities for 804 unique reflexions were obtained from microdensitometer measurements performed by the SRC Service, Daresbury Laboratory, Warrington. After application of the Lorentz and polarization corrections the data were cross correlated and placed on a uniform scale; no absorption correction was applied.

The structure was solved by hand application of the symbolic addition method (Karle & Karle, 1966). The space group does not impose any restriction on molecular symmetry for  $Z = 8$ .

During the initial least-squares refinement, which reduced  $R$  to 7.0%, H atoms were included in the model at fixed calculated positions while other atoms were refined anisotropically. At this stage difference Fourier syntheses and examination of the anisotropic vibration parameters indicated that the crystal structure was partially disordered and contained the two configurations (approximate population ratio 8:1) shown in Fig. 1. Overlap of atomic positions is very close except for atoms O(11) and O(21), which could be located on Fourier maps, while inexact overlap at the positions of N(2) and N(5) could be inferred from the vibration parameters. This disorder was investigated by trial least-squares refinements and by Fourier syntheses. The most satisfactory model was obtained through simultaneous refinement of the atomic parameters of both configurations using the 'slack constraints' facility provided by the least-squares program in the *SHELX 76* system (Sheldrick, 1976). Starting coordinates for O(11), O(21), N(21) and

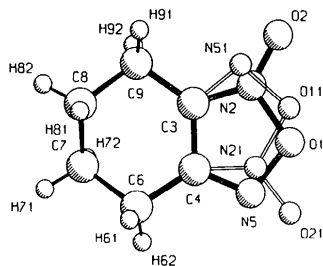


Fig. 1. View of molecule showing atom labels and disordering of the furazan *N*-oxide ring.

Table 1. Atomic coordinates and isotropic thermal parameters with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
O(1)	0.2888 (2)	0.5069 (2)	0.5116 (2)	0.027 (1)*
O(11)	0.2928 (18)	0.4557 (15)	0.5442 (13)	0.033 (4)
O(2)	0.2989 (2)	0.3374 (2)	0.5924 (2)	0.032 (1)*
O(21)	0.2953 (17)	0.6156 (10)	0.4482 (14)	0.040 (5)
N(2)	0.3332 (3)	0.3958 (3)	0.5056 (2)	0.024 (2)*
N(21)	0.3339 (20)	0.5229 (12)	0.4378 (12)	0.022 (5)
N(5)	0.3377 (3)	0.5575 (2)	0.4044 (2)	0.029 (2)*
N(51)	0.3526 (36)	0.3585 (18)	0.5122 (17)	0.062 (12)
C(3)	0.4051 (3)	0.3834 (2)	0.4018 (2)	0.026 (1)*
C(4)	0.4052 (3)	0.4835 (2)	0.3425 (2)	0.026 (1)*
C(6)	0.4774 (3)	0.5023 (2)	0.2207 (2)	0.028 (2)*
C(7)	0.5004 (3)	0.3956 (2)	0.1563 (2)	0.027 (1)*
C(8)	0.5680 (3)	0.3145 (2)	0.2440 (2)	0.027 (1)*
C(9)	0.4714 (3)	0.2847 (2)	0.3529 (2)	0.028 (1)*
H(61)	0.567 (3)	0.534 (2)	0.239 (3)	0.029 (7)
H(62)	0.421 (3)	0.548 (2)	0.171 (3)	0.034 (8)
H(71)	0.560 (3)	0.407 (2)	0.084 (2)	0.024 (6)
H(72)	0.413 (3)	0.368 (2)	0.128 (2)	0.022 (6)
H(81)	0.656 (3)	0.343 (2)	0.281 (2)	0.022 (6)
H(82)	0.596 (3)	0.255 (2)	0.197 (3)	0.036 (7)
H(91)	0.530 (3)	0.250 (2)	0.420 (3)	0.041 (8)
H(92)	0.396 (3)	0.237 (2)	0.325 (3)	0.035 (8)

Occupation factor for O(1), O(2), N(2) and N(5): 0.877 (5)

Occupation factor for O(11), O(21), N(21) and N(51): 0.123 (5)

\*  $U_{eq}$  values for anisotropic atoms.  $U_{eq} = \frac{1}{3}$  (trace of the orthogonal  $U_{ij}$  tensor).

Table 2. Molecular geometry

(a) Intramolecular distances (Å)

O(1)–N(2)	1.465 (4)	O(11)–N(21)	1.47 (2)
O(1)–N(5)	1.392 (3)	O(11)–N(51)	1.40 (3)
O(2)–N(2)	1.229 (3)	O(21)–N(21)	1.23 (2)
N(2)–C(3)	1.314 (3)	N(21)–C(4)	1.32 (2)
C(4)–N(5)	1.312 (4)	C(3)–N(51)	1.32 (2)
C(3)–C(4)	1.413 (3)	O(1)···O(11)	0.73 (2)
C(4)–C(6)	1.491 (3)	N(2)···N(51)	0.51 (2)
C(6)–C(7)	1.527 (3)	N(5)···N(21)	0.56 (2)
C(7)–C(8)	1.530 (4)	C(7)–H(71)	0.97 (3)
C(8)–C(9)	1.531 (4)	C(7)–H(72)	0.95 (3)
C(9)–C(3)	1.491 (3)	C(8)–H(81)	0.99 (3)
C(6)–H(61)	0.97 (3)	C(8)–H(82)	0.94 (3)
C(6)–H(62)	0.95 (3)	C(9)–H(91)	1.01 (3)
		C(9)–H(92)	0.98 (3)

(b) Intramolecular angles (°)

N(2)–O(1)–N(5)	107.7 (2)	N(21)–O(11)–N(51)	102 (1)
O(1)–N(2)–O(2)	117.6 (2)	O(11)–N(21)–O(21)	113 (2)
O(1)–N(2)–C(3)	107.6 (2)	O(11)–N(21)–C(4)	121 (1)
O(2)–N(2)–C(3)	134.8 (3)	O(21)–N(21)–C(4)	126 (1)
N(2)–C(3)–C(4)	105.8 (2)	N(21)–C(4)–C(3)	89 (1)
N(2)–C(3)–C(9)	128.1 (2)	N(21)–C(4)–C(6)	148 (1)
C(3)–C(4)–N(5)	114.1 (2)	C(4)–C(3)–N(51)	128 (1)
C(6)–C(4)–N(5)	123.6 (2)	C(9)–C(3)–N(51)	106 (1)
C(4)–N(5)–O(1)	104.8 (2)	C(3)–N(51)–O(11)	100 (2)
C(9)–C(3)–C(4)	126.1 (2)	H(61)–C(6)–H(62)	112 (2)
C(3)–C(4)–C(6)	122.2 (2)	H(71)–C(7)–H(72)	109 (2)
C(4)–C(6)–C(7)	108.7 (2)	H(81)–C(8)–H(82)	106 (2)
C(6)–C(7)–C(8)	111.9 (2)	H(91)–C(9)–H(92)	111 (2)
C(7)–C(8)–C(9)	112.1 (2)		
C(8)–C(9)–C(3)	108.5 (2)		

(c) Torsion angles (°)

N(2)–C(3)–C(9)–C(8)	–168.5 (3)	N(5)–C(4)–C(6)–C(7)	–161.2 (2)
N(51)–C(3)–C(9)–C(8)	–165 (1)	N(21)–C(4)–C(6)–C(7)	–165 (1)
C(8)–C(9)–C(3)–C(4)	13.0 (3)	C(4)–C(6)–C(7)–C(8)	–49.9 (3)
C(9)–C(3)–C(4)–C(6)	–1.4 (4)	C(6)–C(7)–C(8)–C(9)	65.7 (3)
C(3)–C(4)–C(6)–C(7)	19.4 (3)	C(7)–C(8)–C(9)–C(3)	–43.2 (3)

(d) Distances (Å) of atoms from the least-squares plane defined by O(1), O(2), N(2), N(5), C(3) and C(4)

O(1), 0.006 (2); O(2), –0.003 (2); N(2), –0.001 (3); N(5), –0.004 (3); C(3), 0.004 (2); C(4), –0.002 (2); O(11), 0.05 (2); O(21), 0.06 (2); N(21), 0.04 (2); N(51), 0.08 (3); C(6), 0.006 (3); C(7), –0.461 (3); C(8), 0.292 (3); C(9), –0.011 (3)	
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N(51) were assigned by inspection of difference syntheses and from geometrical considerations. Unfavourable parameter correlations were limited by the following approximate distance constraints:  $r[\text{C}(3)-\text{N}(2)] \simeq r[\text{C}(4)-\text{N}(21)]$ ;  $r[\text{C}(4)-\text{N}(5)] \simeq r[\text{C}(3)-\text{N}(51)]$ ;  $r[\text{O}(1)-\text{N}(2)] \simeq r[\text{O}(11)-\text{N}(21)]$ ;  $r[\text{O}(1)-\text{N}(5)] \simeq r[\text{O}(1)-\text{N}(51)]$  and  $r[\text{N}(2)-\text{O}(2)] \simeq r[\text{N}(21)-\text{O}(21)]$ . Only one variable was used to define the atomic occupation factors such that the sum of occupation factors over the alternative configurations was unity. C atoms and O(1), O(2), N(2) and N(5) were refined anisotropically, other atoms isotropically. An extinction parameter was refined,  $F'_c = F_c(1 - gF_c^2/\sin \theta)$ ; the final value for  $g$  was  $92(6) \times 10^{-7}$ . Additionally, the four most intense reflexions, 202, 221, 302, and 311, were excluded from the least-squares calculations on the basis of severe extinction or film non-linearity effects. The final weighting scheme was  $w^{-1} = 1 + 0.0011(F_o - 10)^2$ ; the final  $R$  factor was 4.2%. A difference Fourier synthesis computed after completion of refinement showed no peaks or troughs outside the range  $\pm 0.2 \text{ e } \text{Å}^{-3}$ . Scattering factors for C, N and O atoms were from Cromer & Mann (1968), those for H atoms were from Stewart, Davidson & Simpson (1965);  $f'$  and  $f''$  corrections were included (Cromer & Liberman, 1970). Calculations were performed using computers of the Edinburgh Regional Computing Centre and using programs written here together with the program systems *SHELX 76* (Sheldrick, 1976), *XRAY 76* (1976), and *PLUTO* (Motherwell, 1976).\*

Atomic parameters are given in Table 1, bond distances and angles, torsion angles and distances of atoms from least-squares planes in Table 2, and intermolecular contacts in Table 3.

\* Lists of structure factors and atomic vibration parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36195 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Intermolecular contacts* (Å)

There are seven intermolecular contacts at distances less than the sum of van der Waals radii (where the van der Waals radii are C, 1.70; N, 1.55; O, 1.52; H, 1.20 Å).

O(11)···H(62 <sup>l</sup> )	2.45 (3)	O(2)···H(62 <sup>l</sup> )	2.68 (3)
O(21)···H(82 <sup>ll</sup> )	2.56 (3)	O(1)···H(62 <sup>l</sup> )	2.72 (3)
O(11)···H(61 <sup>lll</sup> )	2.67 (3)	O(1)···H(71 <sup>lv</sup> )	2.72 (3)
O(11)···H(71 <sup>lv</sup> )	2.68 (3)		

Symmetry code: (i)  $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ ; (ii)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ .

**Discussion.** The disordering of the furazan *N*-oxide ring demands a cautious interpretation of the e.s.d.'s obtained from the least-squares refinement. It would be prudent to multiply the e.s.d.'s given in Tables 1 to 3 by a factor of 2 or 3 to make adequate allowance for the disorder. Unfortunately the effect of this procedure is to prevent decisive comparison between the geometries of the furazan *N*-oxide rings in (1*a*) and (1*b*). Nevertheless, taking the bond lengths for the major component as they stand gives an apparently consistent picture: that the shortening of the O(1)–N(2) bond in (1*b*) by some 0.03 Å (compared to 1*a*) is accompanied by an increase of 0.01 to 0.015 Å in all the other bond lengths around the furazan ring in (1*b*). The exocyclic N(2)–O(2) bond is slightly shorter, by 0.008 Å, in (1*b*) than in (1*a*).

The conformation of the six-membered carbocyclic ring in (1*b*) is constrained by the  $sp^2$  hybridization of the ring-fusion atoms, C(3) and C(4), and by the planarity of the furazan ring. The torsion angle C(9)–C(3)–C(4)–C(6) is  $-1.4(4)^\circ$  and C(6) and C(9) lie very close to the plane of the furazan ring. C(7) and C(8) lie above and below this plane; in cyclohexene this conformational arrangement is known as the half-chair. The only C–C–C angle around the carbocycle that might indicate strain is C(4)–C(3)–C(9),  $126.1(2)^\circ$ ; all other internal angles are close to  $109.5$  or  $120^\circ$  as appropriate.

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