136. Crystal and Molecular Structure of (±)-8,8-Dimethyl-6,7-diazabicyclo[3.3.0]octa-1,6-diene 7-oxide

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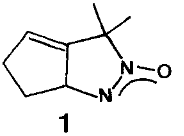
Summary

The exclusive product of thermal rearrangement of (±)-7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene *N*-oxide (**2**) has been identified as the title compound (**1**). The compound crystallizes in the orthorhombic space group *Pbca* (No. 61), with $a = 8.953$ (2), $b = 12.740$ (2), $c = 14.446$ (3) Å; $Z = 8$; $\rho_x = 1.227$ g cm^{-3}. The details of the molecular structure are not unusual, except for a long C–N distance (C(8)–N(7), 1.560 (4) Å). No significant short intermolecular contacts are oserved in the crystal.

Introduction. – The bicyclic diazene-1-oxide **2** has been shown to rearrange thermally, *via* a biradical intermediate, to a single fused isomeric product [1]. The experiments established that the rearrangement is formally equivalent to a [1,3]-sigmatropic shift, but whether the C–N(O) or the C–N bond is cleaved could not be determined. We therefore undertook an X-ray analysis of the title compound **1**.



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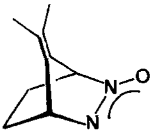

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Experimental Part. – The title compound was prepared in near-quantitative yield by warming a solution of **2** in benzene or acetonitrile to 170° in a sealed *Pyrex* tube. Recrystallization from petroleum ether afforded colorless prisms of **1**, m.p. 55-56°.

A roughly spherical crystal approx. 0.3 mm in diameter was selected and fixed in a glass capillary to limit sublimation. An *Enraf-Nonius* CAD4 diffractometer, fitted with MoK_α source and graphite monochromator, was used for the data collection. Intensities of 1444 independent reflections ($+h$, $+k$, $+l$) in the range $0.1° < \theta < 25°$ were measured by the ω scan method, with stationary background counts before and after each scan. The intensities for $22° < \theta < 25°$ were measured twice, as were several at lower angles. The orientation of the crystal was monitored and corrected during data collection by periodic centering of six axial reflections. The intensities of three standard reflections declined by approx. 9% during data collection. Cell parameters were refined by a least-squares technique using the orientations of 25 strong reflections. Systematically absent reflections in the diffraction data served to identify the space group uniquely.

The SHELX [2] system of programs was used to solve the structure by direct methods. An initial E-map located the C-, N- and O-atoms. Their coordinates were then refined in three least-

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Table 1. *Positional and Vibrational Parameters for* **1**[a])

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.4593 (3)	0.2953 (2)	0.3820 (2)	0.037 (2)	0.045 (2)	0.038 (2)	0.002 (1)	−0.004 (1)	0.000 (1)
C(2)	0.4346 (4)	0.3941 (3)	0.4024 (3)	0.052 (2)	0.047 (2)	0.059 (2)	−0.004 (2)	0.002 (2)	0.004 (2)
C(3)	0.5033 (5)	0.4645 (3)	0.3295 (3)	0.061 (2)	0.045 (2)	0.073 (3)	0.011 (2)	−0.010 (2)	−0.006 (2)
C(4)	0.6170 (5)	0.3917 (3)	0.2821 (3)	0.066 (3)	0.069 (3)	0.056 (2)	0.017 (2)	0.006 (2)	−0.011 (2)
C(5)	0.5518 (4)	0.2823 (3)	0.2962 (2)	0.059 (2)	0.057 (2)	0.035 (2)	0.002 (2)	0.002 (2)	−0.001 (2)
N(6)	0.6556 (3)	0.1958 (2)	0.3176 (2)	0.062 (2)	0.061 (2)	0.048 (2)	−0.001 (2)	0.017 (2)	0.007 (2)
N(7)	0.6033 (3)	0.1478 (2)	0.3874 (2)	0.046 (2)	0.048 (2)	0.049 (2)	−0.001 (1)	0.000 (1)	0.008 (1)
C(8)	0.4553 (4)	0.1914 (2)	0.4295 (2)	0.041 (2)	0.042 (2)	0.038 (2)	−0.001 (1)	0.001 (2)	0.004 (2)
O(9)	0.6610 (3)	0.678 (2)	0.4228 (2)	0.064 (2)	0.062 (2)	0.085 (2)	0.018 (1)	0.002 (2)	0.023 (1)
C(10)	0.3316 (5)	0.1178 (3)	0.3983 (3)	0.054 (2)	0.052 (2)	0.062 (3)	0.003 (2)	−0.009 (2)	−0.008 (2)
C(11)	0.4704 (6)	0.1945 (4)	0.5342 (2)	0.078 (3)	0.065 (3)	0.038 (2)	0.003 (2)	0.005 (2)	−0.008 (3)
H(2)	0.379 (4)	0.420 (3)	0.454 (2)	0.064 (11)					
H(31)	0.553 (4)	0.526 (3)	0.356 (2)	0.058 (10)					
H(32)	0.422 (4)	0.494 (3)	0.286 (2)	0.071 (11)					
H(41)	0.718 (4)	0.398 (3)	0.314 (2)	0.069 (12)					
H(42)	0.643 (4)	0.410 (3)	0.222 (3)	0.086 (13)					
H(5)	0.487 (4)	0.259 (2)	0.244 (3)	0.056 (9)					
H(101)	0.318 (4)	0.114 (3)	0.336 (2)	0.071 (12)					
H(102)	0.348 (4)	0.044 (3)	0.422 (2)	0.072 (12)					
H(103)	0.236 (5)	0.138 (3)	0.429 (2)	0.079 (13)					
H(111)	0.469 (4)	0.123 (3)	0.560 (2)	0.071 (12)					
H(112)	0.555 (4)	0.233 (3)	0.555 (3)	0.081 (14)					
H(113)	0.374 (5)	0.230 (3)	0.562 (3)	0.105 (16)					

[a]) Estimated standard deviations in parentheses. Isotropic vibrational parameters for H-atoms appear under the U_{11} column.

squares cycles, following which a difference *Fourier* synthesis revealed the H-atoms. Further refinement in seven full-matrix least-squares cycles (two with all temperature factors isotropic, and five with anisotropic C, N and O temperature factors) resulted in convergence. In the last cycle none of the 148 parameters shifted by more than half of its e.s.d., and a difference map showed no residual peaks higher than 0.1 e Å^{-3}. Based on 905 reflections with $F > 2\sigma(F)$, the final conventional *R* factor was 0.046.

Table 1 lists the final atomic coordinates and vibration parameters for **1**. Observed and calculated structure factors are available from the authors on request. Atomic scattering factors were taken from *Cromer & Mann* [3] for C, N and O, and from *Cromer* [4] for H.

Results and Discussion. - *Tables 2* and *3* list important bond lengths and angles, respectively. The *Figure*, produced by the program ORTEP [5], is a view of the molecule (*R* enantiomer shown). The two five-membered rings of the molecule each contain four nearly coplanar atoms (C(5)–C(1)–C(2)–C(3) and C(5)–N(6)–N(7)–C(8)) and a fifth atom (C(4) and C(1) respectively) displaced slightly out of that plane. The O-atom lies, as expected, essentially in the N(6)–N(7)–C(8) plane.

Two features of the molecular structure are of interest. One is the long C(8)–N(7) bond. In five of eight previously described crystal structures of diazene 1-oxides (*i.e.* R–N(O)–N–R′) [6], the C–N(O) bond is longer than the C–N bond. In the present case, the difference between the two C–N distances is relatively large (0.085 Å), probably due to steric repulsion from the methyl groups at C(8). That steric interactions can cause substantial lengthening of bonds in similar compounds is suggested by the work of *Baker & Williams* [7]. They determined the crystal structures of 1-cyclohexyl-2-methyldiazene 1-oxide

Table 2. *Interatomic Distances* [Å]a)

C(1)–C(2)	1.312 (5)	C(3)–C(4)	1.538 (6)	N(7)–C(8)	1.560 (4)
C(1)–C(5)	1.500 (4)	C(4)–C(5)	1.525 (5)	N(7)–O(9)	1.251 (3)
C(1)–C(8)	1.492 (4)	C(5)–N(6)	1.475 (4)	C(8)–C(10)	1.520 (5)
C(2)–C(3)	1.514 (5)	N(6)–N(7)	1.269 (3)	C(8)–C(11)	1.519 (5)

a) Estimated standard deviations in parentheses.

Table 3. *Angles and Torsion Angles* [°]a)

C(2)–C(1)–C(5)	112.6 (3)	N(6)–N(7)–C(8)	116.9 (3)
C(2)–C(1)–C(8)	138.1 (3)	N(6)–N(7)–O(9)	124.3 (3)
C(5)–C(1)–C(8)	107.2 (3)	C(8)–N(7)–O(9)	118.8 (3)
C(1)–C(2)–C(3)	110.1 (3)	C(1)–C(8)–N(7)	96.7 (2)
C(2)–C(3)–C(4)	102.8 (3)	C(1)–C(8)–C(10)	115.4 (3)
C(3)–C(4)–C(5)	103.8 (3)	C(1)–C(8)–C(11)	115.7 (3)
C(1)–C(5)–C(4)	102.7 (3)	N(7)–C(8)–C(10)	106.4 (3)
C(1)–C(5)–N(6)	104.9 (3)	N(7)–C(8)–C(11)	108.8 (3)
C(4)–C(5)–N(6)	118.0 (3)	C(10)–C(8)–C(11)	112.1 (3)
C(5)–N(6)–C(7)	107.1 (3)		
C(8)–C(1)–C(2)–C(3)	163	C(1)–C(5)–N(6)–N(7)	17
C(5)–C(1)–C(2)–C(3)	2	C(5)–N(6)–N(7)–C(8)	– 1
C(1)–C(2)–C(3)–C(4)	– 19	C(5)–N(6)–N(7)–O(9)	178
C(2)–C(3)–C(4)–C(5)	27	N(6)–N(7)–C(8)–C(1)	– 15
C(3)–C(4)–C(5)–C(1)	– 26	N(7)–C(8)–C(1)–C(5)	24
C(3)–C(4)–C(5)–N(6)	– 141	N(7)–C(8)–C(1)–C(2)	– 137

a) Estimated standard deviations in parentheses.

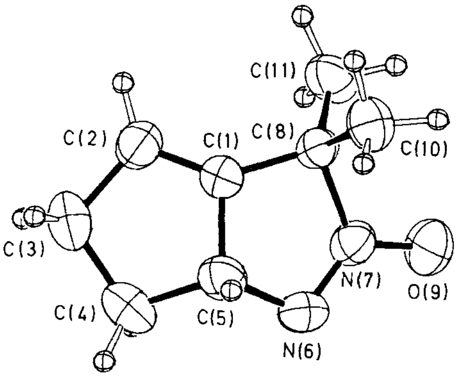
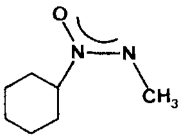


Figure. *Molecular structure showing atom numbering*

(**3**) and 2-cyclohexyl-1-methyldiazene 1-oxide (**4**), and found the cyclohexyl-N bond the longer of the two C–N bonds in both cases. In the structure of 2,3-diazabicyclo[2.2.2]oct-2-ene 2-oxide (**5**) [8], where such steric interactions are expected to be weaker, the two C–N distances differ by only 0.015 Å (with C–N(O) again longer than C–N).



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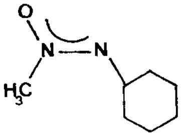

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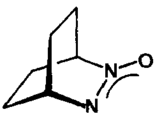

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The second noteworthy aspect of the molecular geometry is the distortion of valence angles at atoms C(1) and C(8). Angle C(1)–C(8)–N(7) appears to be unusually small (96.7 (2)°) for a bond angle at tetrahedral C-atom. But as this angle is included in a five-membered ring containing three sp^2-hybridized atoms, some distortion is to be expected. The crystal structures of two derivatives of pyrroline-1-oxyl (which contains a similar five-membered ring) [9] [10] also show C–C–N angles of less than 100°. The geometrical restrictions imposed by the two rings are probably responsible for the angular and out-of-plane distortion at C(1) as well.

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