

molecules. These nearest-neighbor interactions are between non-symmetry related molecules forming parallel chains along the *a* axis of the crystal. The distance O(7)–N(19) is 2.875 Å and the distance O(17)–N(9'), where N(9') is related to N(9) by a unit translation along the *a* axis, is 2.905 Å. Both of these distances are approximately equal to the sum of the normally accepted van der Waals radii for nitrogen and oxygen atoms.

This work was supported by a grant from the Robert A. Welch Foundation of Houston, Texas. The computer calculations were done at the Common Research Computer Facility located in the Texas Medical Center and supported by U.S.P.H. Grant FR-00254.

Acta Cryst. (1970). **B26**, 1198

Refinement and location of the hydrogen atoms in the nitroxide 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl.

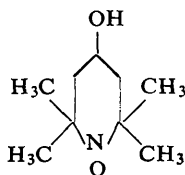
By LAWRENCE J. BERLINER*, *Laboratory of Molecular Biophysics, Department of Zoology, Oxford University, Oxford, England and Department of Chemistry, Stanford University, Stanford, California 94305, U.S.A.*

(Received 7 November 1969)

The structure of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl as determined by Lajzėrowicz-Bonneteau has been refined using data from a four-circle diffractometer. While the original work yielded a structure with an *R* value of 0.12 using isotropic least-squares refinement of the non-hydrogen atoms, the results of the current study have yielded (1) the positions and isotropic thermal parameters for all of the hydrogen atoms, (2) the anisotropic thermal parameters of the non-hydrogen atoms, and (3) a refinement of the entire structure to an *R* value of 0.055. The only major significant differences observed were (1) a large decrease in the C–N–C bond angle, and (2) a moderate decrease in the $\begin{matrix} \text{C} \\ \diagup \\ \text{N-O} \\ \diagdown \\ \text{C} \end{matrix}$ 'out of plane' angle to a value more consistent with expected configurations derived from anisotropic hyperfine interaction measurements.

Introduction

The structure of the nitroxide radical 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl was determined from photographic data by Lajzėrowicz-Bonneteau (1968) (hereafter referred to as L-B, 1968).



* Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CHU, S. S. C., JEFFREY, G. A. & SAKURAI, T. (1962). *Acta Cryst.* **15**, 661.
- DICKERSON, R. E. (1959). *Acta Cryst.* **12**, 610.
- PALENIK, G., DONOHUE, J. & TRUEBLOOD, K. (1968). *Acta Cryst.* **B24**, 1139.
- POLYNOVA, T. N., BOKII, N. G. & PORAI-KOSHITS, M. A. (1965). *Zh. Strukt. Khim.* **6**, 878.
- TROTTER, J. (1960). *Acta Cryst.* **13**, 86.

The structure of this compound as reported here has been determined using diffractometer methods. The interest in this structure stems from its properties as a 'spin label' in structure-function studies of biological molecules (Hamilton & McConnell, 1968). In view of the unexpected value for the $\begin{matrix} \text{C} \\ \diagup \\ \text{N-O} \\ \diagdown \\ \text{C} \end{matrix}$ 'out of plane' angle of 21° as found by L-B (1968), it was decided to carry out a full refinement of the structure.

Experimental

The compound was prepared by the method of Brière, Lemaire & Rassat (1965), but was crystallized from hexane/chloroform, yielding crystals of similar morphology to other preparations (L-B, 1968).

Table 1. *Summary of refinement procedure*

The reported *R* values are determined using all reflections with no special treatment of weak reflections.

Parameters refined	Initial <i>R</i>	Final <i>R</i>	Number of cycles
<i>x</i> , <i>y</i> , <i>z</i> , <i>B</i> _{iso} non-hydrogen atoms		0.12 (L-B, 1968)	
<i>x</i> , <i>y</i> , <i>z</i> , <i>B</i> _{iso} non-hydrogen atoms	0.244	0.150	4
<i>x</i> , <i>y</i> , <i>z</i> , <i>B</i> _{ij} non-hydrogen atoms	0.150	0.0934	3
As above, including hydrogen positions and <i>B</i> _{iso} values	0.0934	0.0551*	3

* Omitting the very strong 001, 020 and 110 reflections, *R*=0.0471.

X-ray data were collected on a Hilger & Watts four-circle diffractometer using molybdenum radiation ($\lambda_{K\alpha} = 0.711 \text{ \AA}$). Cell dimensions were determined from diffractometer measurements. The crystal density was measured by flotation in carbon tetrachloride/chloroform. The crystallographic data are listed below:

2,2,6,6-Tetramethyl-4-piperidinol-1-oxyl, $C_9H_{18}NO_2$.

M.W. 172.24. Space group, Cm , $Z=2$

$a = 7.10 \pm 0.01 \text{ \AA}$

$b = 14.00 \pm 0.02$

$c = 5.84 \pm 0.01$

$\beta = 119.8 \pm 0.3^\circ$

$V = 503.7 \text{ \AA}^3$

$D_{\text{calc}} = 1.14 \text{ g.cm}^{-3}$

$D_{\text{exp}} = 1.13 \text{ g.cm}^{-3}$

Table 2. Observed and calculated structure amplitudes ($\times 30$)

h	k	l	F_o	F_c	ΔF	h	k	l	F_o	F_c	ΔF
0	0	0	0.641 745	-0.46 45	-0.20 19	L F0B FCA	0	0	0	0.641 745	-0.46 45
0	0	1	1.714 705	-0.52 50	-0.19 20	L F0B FCA	0	0	1	1.714 705	-0.52 50
0	0	2	3.006 455	-0.16 76	-0.14 03	L F0B FCA	0	0	2	3.006 455	-0.16 76
0	1	0	1.955 995	1.165 135	-1.01 40	-3.52 55	-5.103 100	-7.02 59	-3.57 97	-4.109 116	-5.36 14
0	1	1	3.245 376	0.52 52	0.57 58	-0.02 60	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	2	3.165 138	0.67 05	1.46 44	-1.21 18	-3.72 69	-5.150 147	-5.16 19	-2.134 131	-3.26 81
0	1	3	4.150 204	0.60 42	0.5 0	0.26 24	0.80 120	-0.119 116	-0.159 122	-1.03 92	-2.36 40
0	1	4	5.124 119	0.67 05	3.36 34	1.103 97	-1.36 42	-3.196 173	-3.207 280	0.41 47	-1.47 69
0	1	5	6.10 110	M_{HkL} 1, 3	0.26 24	2.129 170	0.80 120	-0.119 116	-0.159 122	-1.03 92	0.67 05
0	1	6	7.076 100	M_{HkL} 1, 3	3.72 70	1.21 24	-1.03 88	-1.72 95	2.41 45	1.71 27	0.67 05
0	1	7	8.051 900	M_{HkL} 1, 3	4.41 41	3.46 46	0.130 165	0.103 181	0.103 181	0.103 181	0.67 05
0	1	8	9.026 800	M_{HkL} 1, 3	5.10 50	4.36 39	1.126 124	1.5 23	M_{HkL} 6, 4	M_{HkL} 7, 7	0.67 05
0	1	9	1.001 835	-0.76 79	-1.36 39	M_{HkL} 2, 12	2.52 57	2.16 10	L F0B FCA	L F0B FCA	0.67 05
0	1	10	1.976 874	-0.12 76	-0.46 45	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	11	2.951 913	-0.16 76	-0.14 03	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	12	3.926 952	-0.20 76	-0.16 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	13	4.901 991	-0.24 76	-0.18 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	14	5.876 030	-0.28 76	-0.20 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	15	6.851 069	-0.32 76	-0.22 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	16	7.826 108	-0.36 76	-0.24 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	17	8.801 147	-0.40 76	-0.26 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	18	9.776 186	-0.44 76	-0.28 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	19	10.751 225	-0.48 76	-0.30 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	20	11.726 264	-0.52 76	-0.32 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	21	12.701 303	-0.56 76	-0.34 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	22	13.676 342	-0.60 76	-0.36 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	23	14.651 381	-0.64 76	-0.38 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	24	15.626 420	-0.68 76	-0.40 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	25	16.601 459	-0.72 76	-0.42 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	26	17.576 498	-0.76 76	-0.44 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	27	18.551 537	-0.80 76	-0.46 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	28	19.526 576	-0.84 76	-0.48 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	29	20.501 615	-0.88 76	-0.50 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	30	21.476 654	-0.92 76	-0.52 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	31	22.451 693	-0.96 76	-0.54 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	32	23.426 732	-1.00 76	-0.56 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	33	24.401 771	-1.04 76	-0.58 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	34	25.376 810	-1.08 76	-0.60 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	35	26.351 849	-1.12 76	-0.62 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	36	27.326 888	-1.16 76	-0.64 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	37	28.301 927	-1.20 76	-0.66 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	38	29.276 966	-1.24 76	-0.68 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	39	30.251 005	-1.28 76	-0.70 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	40	31.226 044	-1.32 76	-0.72 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	41	32.201 083	-1.36 76	-0.74 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	42	33.176 122	-1.40 76	-0.76 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	43	34.151 161	-1.44 76	-0.78 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	44	35.126 200	-1.48 76	-0.80 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	45	36.101 239	-1.52 76	-0.82 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	46	37.076 278	-1.56 76	-0.84 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	47	38.051 317	-1.60 76	-0.86 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	48	39.026 356	-1.64 76	-0.88 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	49	40.001 395	-1.68 76	-0.90 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	50	40.976 434	-1.72 76	-0.92 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	51	41.951 473	-1.76 76	-0.94 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	52	42.926 512	-1.80 76	-0.96 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	53	43.901 551	-1.84 76	-0.98 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	54	44.876 590	-1.88 76	-1.00 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	55	45.851 629	-1.92 76	-1.02 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	56	46.826 668	-1.96 76	-1.04 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	57	47.801 707	-2.00 76	-1.06 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	58	48.776 746	-2.04 76	-1.08 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	59	49.751 785	-2.08 76	-1.10 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	60	50.726 824	-2.12 76	-1.12 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	61	51.701 863	-2.16 76	-1.14 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	62	52.676 902	-2.20 76	-1.16 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	63	53.651 941	-2.24 76	-1.18 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	64	54.626 980	-2.28 76	-1.20 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	65	55.601 019	-2.32 76	-1.22 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	66	56.576 058	-2.36 76	-1.24 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	67	57.551 097	-2.40 76	-1.26 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	68	58.526 136	-2.44 76	-1.28 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	69	59.501 175	-2.48 76	-1.30 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	70	60.476 214	-2.52 76	-1.32 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	71	61.451 253	-2.56 76	-1.34 76	0.26 24	0.98 94	0.88 88	-0.109 106	-3.31 15	-0.47 87
0	1	72	62.426 292	-2.60 76	-1.36 76	0.26 24	0.98 94				

Table 3. Fractional atomic coordinates and thermal parameters

	The thermal parameters β_{ij} are coefficients in the temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.									
	$x/a(10^4\sigma)$	$y/b(10^4\sigma)$	$z/c(10^4\sigma)$	$B(\sigma^2)$	$\beta_{11}(10^4\sigma)$	$\beta_{22}(10^4\sigma)$	$\beta_{33}(10^4\sigma)$	$\beta_{12}(10^4\sigma)$	$\beta_{13}(10^4\sigma)$	$\beta_{23}(10^4\sigma)$
O(1)	-0.0090 (6)	0.0	-0.0213 (13)	0.0210 (9)	0.0121 (4)	0.0457 (17)	0.0	0.0203 (11)	0.0	0.0
C(1)	0.1653 (8)	0.0	-0.0755 (12)	0.0148 (9)	0.0069 (3)	0.0296 (14)	0.0	0.0123 (9)	0.0	0.0
C(2)	0.1638 (8)	0.0	-0.2286 (11)	0.0237 (9)	0.0534 (2)	0.0351 (12)	0.0024 (3)	0.0146 (8)	0.0	0.0005 (4)
C(3)	0.3637 (8)	0.0878 (2)	-0.2610 (10)	0.0245 (7)	0.0040 (1)	0.0299 (10)	-0.0004 (3)	0.0150 (7)	-0.0004 (3)	-0.0004 (3)
C(4)	0.5634 (9)	0.0951 (2)	-0.0016 (12)	0.0308 (11)	0.0067 (2)	0.0421 (16)	-0.0050 (4)	0.0175 (11)	0.0	-0.0061 (5)
C(5)	0.3176 (11)	0.1657 (2)	-0.4837 (12)	0.0487 (16)	0.0047 (2)	0.0468 (17)	0.0003 (4)	0.0282 (14)	0.0	0.0020 (4)
N	0.4122 (8)	0.0	-0.3376 (7)	0.0180 (7)	0.0047 (2)	0.0236 (10)	0.0	0.0118 (7)	0.0	0.0
O(2)	0.5512 (7)	0.0	-0.4190 (10)	0.0230 (8)	0.0073 (2)	0.0348 (13)	0.0	0.0190 (8)	0.0	0.0
H(01)	-0.1284 (124)	0.0	-0.1807 (156)	6.0 (1.5) Å ²						
H(1)	0.2983 (98)	0.0	0.0903 (112)	3.4 (1.1)						
H(2-1)	0.0485 (84)	0.0804 (34)	0.3963 (104)	4.9 (1.0)						
H(2-2)	0.1582 (73)	0.1495 (35)	-0.1402 (97)	4.8 (1.0)						
H(4-1)	0.5366 (91)	0.1944 (36)	0.0352 (123)	6.2 (1.1)						
H(4-2)	0.6726 (80)	0.1310 (34)	-0.0220 (96)	4.8 (1.0)						
H(4-3)	0.6024 (78)	0.0898 (35)	0.1451 (103)	4.7 (1.0)						
H(5-1)	0.1991 (92)	0.1465 (35)	-0.6496 (116)	5.1 (1.0)						
H(5-2)	0.4400 (81)	0.1700 (32)	-0.5007 (95)	4.7 (0.9)						
H(5-3)	0.2710 (106)	0.2354 (44)	-0.4523 (122)	8.4 (1.4)						

The space group *Cm* has 4 asymmetric units in the unit cell; however, in this special case, the crystallographic mirror plane *m* coincides with the molecular mirror plane (through the O-C and N-O bonds); thus, there are only two molecules per unit cell.

The intensities of the 640 reflections measured were treated with a data processing program written for the KDF-9 computer by Mrs Eleanor Dodson of the Chemical Crystallography Laboratory, Oxford. Absorption corrections were assumed to be sufficiently small to neglect.

Refinement of the structure

Starting with the coordinates and isotropic temperature factors of L-B (1968), the structure (without hydrogen atoms) was refined first with isotropic thermal parameters, then anisotropic parameters to an *R* index

$$(\sum ||F_o| - |F_c|| / \sum |F_o|)$$

of 0.093. The least squares program used was written by Dr G. A. Mair for the Elliott 803 computer at Oxford. It utilizes the block-diagonal approximation and a weighting scheme defined by

$$w = 1 / \{1 + (F_o - b)^2 / a^2\}$$

where *a* and *b* are constants selected to discriminate against the very weak and very strong reflections (Rollett, 1961). The values chosen were *a*=2 and *b*=3, on an absolute scale. At this point, a difference Fourier synthesis revealed the positions of the hydrogen atoms.

The next stage of the refinement was done with a modification of the *ORFLS* program of Busing, Martin & Levy (1962) called *SUFLS*, written for the Stanford University IBM 360/67 computer. After 3 cycles of full-matrix refinement on the entire structure, refining isotropically on the hydrogen atoms and anisotropically on the other atoms, a limiting *R* index of 0.055 was reached. The same weighting scheme as above was used. The scattering factors for C, O, and N were taken from *International Tables for X-ray Crystallography* (1962) and the values for H were taken from Stewart, Davidson & Simpson (1965). Table 1 summarizes the refinement scheme. The observed structure amplitudes and final calculated structure amplitudes are listed in Table 2.

Description and discussion of the structure

The final atomic coordinates and thermal parameters are tabulated in Table 3. The numbering system for the atoms is shown in Fig. 1 and an *ORTEP* (Johnson, 1965) stereographic drawing of the molecule is shown in Fig. 2. In all cases the labeling of atoms is consistent with that of L-B (1968).

The average differences from the values reported earlier (L-B, 1968) are of the order of 1-2% in bond lengths. It should be noted that a value of 1.291 ± 0.007 Å was found for the N-O bond length (L-B, 1968: 1.26 ± 0.035 Å), falling somewhat closer to the distances found in other nitroxides: di-*t*-butyl nitroxide, 1.28 ± 0.03 Å (Andersen & Andersen, 1966), 2,2,5,5-tetramethyl-3-carboxyl-pyrroline-1-oxyl, 1.27 ± 0.01 Å (Kruger & Boeyens, 1970), and caryophyllene iodinitrosite, 1.308 ± 0.021 Å (Hawley, Ferguson & Robertson, 1968).

The C(3)-N-C(3') interatomic angle was found to be $125.4 \pm 0.5^\circ$, a significant change from the value of $134 \pm 2^\circ$

Table 4. Bond lengths and bond angles involving hydrogen atoms

A few pertinent non-bonded distances related to the hydrogen bond are included and are denoted with . . .

O(1)——H(O1)	0.89 ± 0.08 Å		
H(O1i)···O(2ii)	1.99 ± 0.08	C(1)——O(1)——H(O1)	104.3 ± 5.0°
C(1)——H(1)	0.96 ± 0.06		
C(2)——H(2-1)	0.92 ± 0.05	O(1i) ——H(O1i)···O(2ii)	152.8 ± 7.1
C(2)——H(2-2)	1.02 ± 0.05	H(O1i)···O(2ii)——N _{II}	124.0 ± 2.3
C(4)——H(4-1)	1.01 ± 0.05	O(1)——C(1)——H(1)	107.7 ± 2.5
C(4)——H(4-2)	0.84 ± 0.05	H(2-1)——C(2)——H(2-2)	113.5 ± 4.0
C(4)——H(4-3)	0.92 ± 0.05	H(4-1)——C(4)——H(4-2)	104.8 ± 4.6
C(5)——H(5-1)	0.95 ± 0.06	H(4-1)——C(4)——H(4-3)	109.5 ± 4.8
C(5)——H(5-2)	0.92 ± 0.05	H(5-1)——C(5)——H(5-2)	108.1 ± 4.6
C(5)——H(5-3)	1.07 ± 0.06	H(5-1)——C(5)——H(5-3)	103.8 ± 4.6

reported by L-B (1968). This smaller angle might be expected for strained closed-ring systems such as this, and in fact correlates well with the data on a related structure (Hawley, Ferguson & Robertson, 1968).

Conclusive evidence was found for hydrogen bonding between the hydroxyl group proton of one molecule and the oxygen atom on the nearest neighbor nitroxide group as inferred by L-B (1968). The resultant H(O1i)···O(2ii) distance of 1.991 Å and O(1i)···O(2ii) distance of 2.817 Å (see Table 4) fall well into the region of hydrogen bonding contact distances (Pauling, 1960). The O(1i)–H(Oi)–O(2ii) angle, however, appears to deviate from linearity by 27° (see Table 4).

The other significant change observed is the decrease in the $\begin{matrix} \text{C} \\ \diagup \\ \text{N-O(2)} \\ \diagdown \\ \text{C} \end{matrix}$ 'out of plane' angle from 21° (L-B, 1968) to 15.8 ± 0.8°. This angle is defined as the acute angle between the N–O(2) bond and the C(3)–N–C(3') plane. The value of the isotropic electron–nuclear hyperfine interaction (direct spin coupling between the free electron and the nitrogen nucleus) indicates that the odd electron orbital is of almost pure *p*-character (Griffith, Cornell & McConnell, 1965). This would suggest that the C(3)–N–C(3') covalent bond



configuration around the nitrogen atom should be almost planar in order that the odd electron $2p\pi$ orbital be orthogonal to the other orbitals (Hamilton & McConnell, 1968). An approximate calculation of the isotropic hyperfine coupling constant as a function of the N–O 'out of plane' angle, as based on an approximation treatment of Atkins & Symons (1967), indicates that the observed coupling constant (~16 gauss) is more consistent with the smaller angle of 15.8°.

The remarkable resistance to reduction or dimerization, and the stability of the nitroxide group towards several organic reagents, are accounted for, in part, by the steric hindrance of the adjacent *t*-alkyl groups (Hofmann & Henderson, 1961). Table 5 lists several intramolecular distances between atoms on the flanking 2,2,6,6-methyl groups and the N–O group. One must be aware of the fact, however, that in analogous piperidines, the N–H group has been modified with several primarily linear aliphatic groups with no difficulties (Young, 1960). Since the environment of the N–H group is very likely to be identical to that of the N–O group in analogous compounds, it is the opinion of the author that, in fact, the major contribution to the stability of the nitroxide group is in the intrinsic stability of the N–O three-electron bond (Linnett, 1961).

Table 5. Nitrogen–methyl hydrogen non-bonded distances

H(4-1)–N	3.32 ± 0.05 Å
H(4-2)–N	2.61 ± 0.04
H(4-3)–N	2.75 ± 0.05
H(5-1)–N	2.66 ± 0.05
H(5-2)–N	2.61 ± 0.05
H(5-3)–N	3.41 ± 0.06

The author wishes to thank Professor D. C. Phillips for providing the facilities for the major portion of this work during 1967–68. His colleagues at the Laboratory of Molecular Biophysics were very helpful, especially Dr E. N. Baker, who carried out most of the diffractometer measurements. The work at Oxford was done during the tenure of a British–American Research Fellowship of the British Heart Foundation and the American Heart Association.

The author also wishes to thank Professor H. M. McConnell for providing the facilities for the completion of this work during 1968–69. Especial acknowledgement is due to Dr Paul Simpson and his research group for their continuous assistance. In particular, Dr T. E. Hopkins and J. Becker were extremely helpful. The work at Stanford was done during the tenure of an Advanced Research Fellowship of the American Heart Association.

References

- ANDERSEN, B. & ANDERSEN, P. (1966). *Acta Chem. Scand.* **20**, 2728.
- ATKINS, P. W. & SYMONS, M. C. R. (1967). *The Structure of Inorganic Radicals*, pp. 22, 254. Amsterdam: Elsevier.
- BRIÈRE, R., LEMAIRE, H. & RASSAT, A. (1965). *Bull. Soc. chim. Fr.* p. 3273.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Report ORNRL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- GRIFFITH, O. H., CORNELL, D. W. & MCCONNELL, H. M. (1965). *J. Chem. Phys.* **43**, 2909.
- HAMILTON, C. L. & MCCONNELL, H. M. (1968). *Structural Chemistry and Molecular Biology*, Ed. A. RICH and N. DAVIDSON, p. 115. San Francisco: Freeman.
- HAWLEY, D. M., FERGUSON, G. & ROBERTSON, J. M. (1968). *J. Chem. Soc. B*, p. 1255.
- HOFMANN, A. V. & HENDERSON, A. T. (1961). *J. Amer. Chem. Soc.* **83**, 4671.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

- JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal-Structure Illustrations*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KRUGER, G. J. & BOEYENS, J. C. A. (1970). *Acta Cryst.* In the press.
- LAJZÉROWICZ-BONNETEAU, P. J. (1968). *Acta Cryst.* B24, 196.
- LINNETT, J. W. (1961). *J. Amer. Chem. Soc.* 83, 2643.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ch. 12. Ithaca: Cornell Univ. Press.
- ROLLETT, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Analysis*. Oxford: Pergamon Press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175.
- YOUNG, E. H. P. (1960). *Brit. Patent*, 834,290.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J.N.King, 13 White Friars, Chester CH1 1NZ, England).

A Symposium on Crystal Structure and Chemical Bonding

Twente, The Netherlands, 3-6 August 1971

The Netherlands National Committee for Crystallography (F.O.M.R.E.) is arranging a symposium on Crystal Structure and Chemical Bonding from 3 to 6 August 1971 at the Technological University, Twente, Enschede, The Netherlands. Topics to be covered will include structure analysis and molecular spectroscopy, intermolecular forces, electron densities, the accuracy of results, the general theory of bonding and interactions, and the comparison of results of different methods. Registration will be accepted until 1 February 1971, but the total number of participants will have to be limited to 150.

Inquires should be addressed to the organizing secretary, Dr A. Schuyff, Laboratory for Crystal Chemistry, University of Utrecht, Utrecht, The Netherlands.

ICSU Abstracting Board Publications

The 1969 issues of two annual publications detailing the activities of those Scientific Unions (including the International Union of Crystallography) which are members of the International Council of Scientific Unions (ICSU) and the activities of the Committees and Commissions of ICSU

have been published recently by the ICSU Abstracting Board and may be purchased from the ICSU AB Secretariat, 17 rue Mirabeau, Paris 16e, France. The title of one publication, *Tentative List of Publications of ICSU Scientific Unions, Special and Scientific Committees and Commissions of ICSU, Year 1969, and Corrections and Additions to the 1968 List*, is self-explanatory. The other publication, entitled *Survey of the Activities of the ICSU Scientific Unions, Special and Scientific Committees and Commissions of ICSU in the Field of Scientific Information during the Year 1969*, presents information under the following headings: Name of union, commission, committee, or working group; President/chairman (name and address); Secretary (name and address); Members (names and countries); Date of creation; Periodicity of meetings; and publication of minutes of meetings. A general description is given of the activities and a listing of 1969 publications. Particular attention is given to those bodies dealing with the following topics: notations, symbols, units, nomenclature, terminology, standards, bibliographies, abstracts, review articles, classification, and publication of data.

The purpose of the ICSU AB surveys is to make the activities of the Scientific Unions and ICSU bodies in the field of scientific information more widely known in the scientific community, and to strengthen cooperation between those bodies working in similar fields.