

**THE CRYSTAL AND MOLECULAR STRUCTURE OF THE
POTASSIUM SALT OF
2,2,5,5-TETRAMETHYL-3-CARBOXYPYRROLINE-1-OXYL**

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The crystal structure of the potassium salt of 2,2,5,5-tetramethyl-3-carboxypyrroline-1-oxyl (I), which is a free radical of the nitroxide type, has been determined by three-dimensional X-ray methods. The unit cell contains two crystallographically different types of molecule, one of which lies with its five-membered ring entirely in a mirror plane and is therefore perfectly flat. Molecules of the second type lie in general positions and are also flat to within experimental error.

Materials and Methods.—The preparation of I was first described by Rozantzev and Krinitzkaya.¹ Our sample was synthesized by Dr. Carole L. Hamilton of the Stauffer Laboratory, Stanford University, and recrystallized from water. The initial X-ray photographs of the needle-shaped crystals indicated that they were hexagonal. Non-space group absences on higher layer-line Weissenberg photographs as well as a slight doubling of spots suggested, however, that each crystal consisted of three orthorhombic individuals, trilled to give apparent hexagonal symmetry.² This requires an axial ratio of $\sqrt{3}:1$, which was indeed found on examination of a single crystal fragment obtained by splitting a crystal along its needle axis. The crystals are slightly hygroscopic, and therefore a single needle was sealed with some calcium chloride into a thin-walled glass capillary for the X-ray work. The cell data were established as follows from a set of oscillation and Weissenberg photographs:

$$\begin{aligned}a &= 20.67 \text{ \AA}, \\b &= 7.05 \text{ \AA}, \\c &= 12.05 \text{ \AA}.\end{aligned}$$

The measured density of 1.32 gm cm^{-3} can only be explained if the unit cell contains six molecules of I and two molecules of water. For this composition $\rho(\text{calc.}) = 1.30 \text{ gm cm}^{-3}$. The only systematic absences were in $h0l$ for $h + l = 2n$. On this basis either of the space groups $Pmn2_1$ or $Pmnm$ could be assigned.

The intensities of 1613 hkl reflections (including 269 unobserved) were measured visually by using the standard multiple film equi-inclination Weissenberg technique³ with $\text{CuK}\alpha$ (Ni filter) radiation. All standard corrections were applied, a suitable computer program being used,⁴ and a three-dimensional Patterson synthesis was calculated.⁵ A solution was found to exist only for the noncentrosymmetric space group $Pmn2_1$, no. 31 in the International Tables.⁶ A value of $1/2J_{\text{min}}$ was therefore assigned to all unobserved reflections,⁷ and a three-dimensional Fourier synthesis was calculated⁵ with all phases based on the positions of the two potassium atoms as derived from the Patterson synthesis. The positions of all other atoms were found directly from this Fourier map. Preliminary refinement of the structure was done by the method of least squares with a full matrix computer program^{8, 9} until all parameter shifts were less than 0.1 of their estimated standard deviations. At this stage the discrepancy defined as $R = \Sigma \Delta F / \Sigma F_0$ was 0.148 for all reflections. The final atomic parameters and individual isotropic temperature factors with their estimated standard deviations are given in Table 1.

Description of the Structure.—In the noncentrosymmetric space group $Pmn2_1$ the z -coordinate of any motif is indeterminate. In this structure it was fixed by assigning $z = 0$ to the potassium atom in the general position, having Wyckoff

TABLE 1. Fractional atomic coordinates and individual temperature factors of the atoms in one asymmetric unit and their estimated standard deviations.

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
K	0	0.6769	0.9547	1.87	C'2	0.182	0.667	0.191	1.7
C1	0	0.0009	0.0005	0.09	C'3	0.0007	0.003	0.001	0.3
C2	0	0.019	0.604	1.9	C'4	0.208	0.514	0.233	2.6
C3	0	0.004	0.002	0.4	C'5	0.0008	0.003	0.002	0.3
C4	0	0.193	0.674	1.7	C'6	0.265	0.558	0.308	3.2
C5	0	0.004	0.002	0.4	C'7	0.0009	0.003	0.002	0.4
C6	0	0.350	0.616	2.5	C'8	0.125	0.668	0.106	2.2
C7	0	0.005	0.002	0.5	C'9	0.0007	0.003	0.001	0.3
C8	0	0.311	0.484	2.5	0'1	0.330	0.474	0.269	5.3
C9	0	0.004	0.002	0.5	0'2	0.001	0.004	0.002	0.6
01	0	0.195	0.803	2.2	0'3	0.243	0.515	0.441	5.2
02	0	0.004	0.002	0.4	N'	0.001	0.004	0.002	0.4
03	0	0.388	0.429	4.5	OH ₂ O	0.252	0.961	0.002	0.5
K'	0.063	0.004	0.002	4.5		0.001	0.004	0.131	3.6
C'1	0.001	0.004	0.002	0.5		0.171	0.978	0.002	0.4
	0.062	0.903	0.615	3.9		0.001	0.004	0.303	3.7
	0.001	0.004	0.002	0.4		0.310	0.861	0.002	0.4
	0	0.009	0.397	4.6		0.0007	0.002	0.352	4.4
	0	0.004	0.002	0.5		0.106	0.826	0.001	0.3
	0	0.030	0.845	2.1		0.006	0.002	0.075	3.5
	0	0.003	0.001	0.3		0.104	0.511	0.001	0.3
	0	0.348	0.850	2.1		0.0006	0.002	0.086	3.1
	0	0.003	0.001	0.3		0.266	0.756	0.001	0.3
	0	0.121	0.486	3.0		0.0006	0.002	0.303	2.4
	0	0.004	0.002	0.4		0	0.097	0.167	6.9
	0.0925	0.1712	0	2.02		0.005	0.003	0.003	0.7
	0.0002	0.0006	0	0.07					
	0.214	0.846	0.228	2.4					
	0.0008	0.003	0.002	0.3					

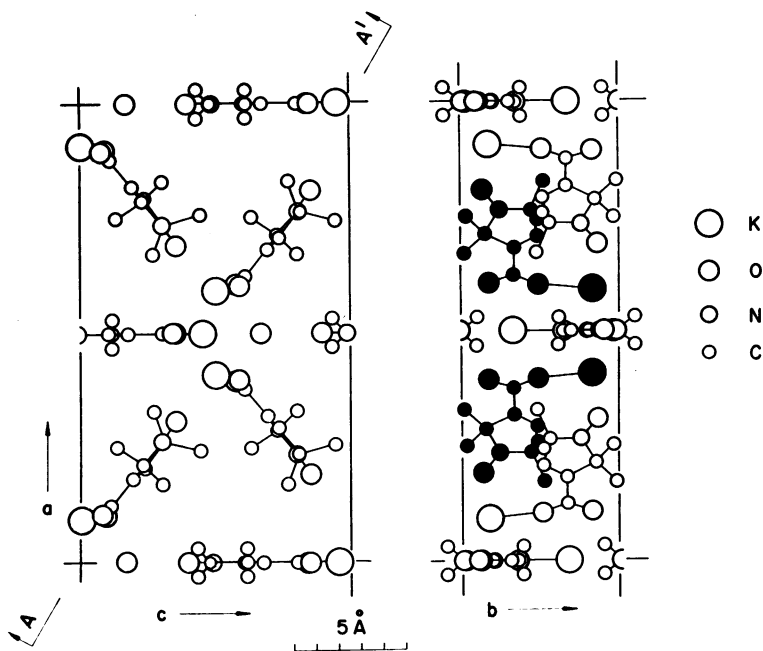


FIG. 1.—The (010) and (001) projections of the contents of the unit cell. For the sake of clarity, one molecule of each overlapping pair is shown in black.

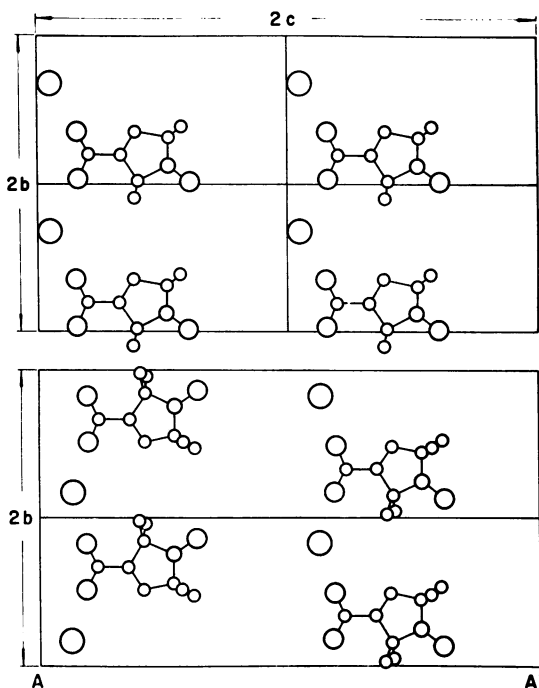


FIG. 2.—A comparison of the population of the (100) and (101) planes.

notation *b*. The (010) and (001) projections of the corresponding structure are shown in Figure 1. The total of six molecules is seen to be made up of two in special positions on crystallographic mirror planes and four others, not related by symmetry to the former two, in general positions. The water molecules also lie in the mirror planes. This uncommon situation allows the determination of two independent molecular structures of the same compound in one analysis.

The molecules in general positions are seen to lie almost parallel to (101) planes so that in (010) projection there is a pseudo threefold symmetry point at $(1/6, -, 1/2)$. This provides the only possible explanation of the observed trilling although the (100) and (101) planes are not very similarly populated, as shown in Figure 2. Only alternate rows of molecules in (100) planes can match similar rows in (101) planes after some rearrangement. This shows that a perfect match of the (101) faces of any individual with the (100) faces of the two other individuals is not a necessary condition for the formation of a triplet crystal.

The water molecules in the structure appear to be zeolitic in nature and to occupy the two voids per unit cell which occur among molecules of I. Slight disorder in the positions of the water molecules as indicated by the high-temperature factor of the oxygen atom (Table 1) also suggests that the water molecules are not bound by chemical forces. The distance between an oxygen atom in a water molecule and a nitroxide oxygen atom in the mirror plane is, however, only 2.84 Å. Hydrogen bonding between the water and a nitroxide group is thus possible.

Discussion of the Structure.—The structures of nitroxide radicals are important in the detailed interpretation of various experimental results obtained in studies

TABLE 2. *Deviations from planarity of the pyrroline ring in general position and the distances of the associated atoms from this plane.*

C ₁ '	0.000 Å	K'	-0.838 Å
C ₂ '	-0.004	C ₅ '	-0.077
C ₃ '	0.006	O ₁ '	-0.061
C ₄ '	-0.005	O ₂ '	-0.075
N'	0.003	O ₃ '	-0.058

TABLE 3. *Intramolecular bond lengths.**

Bond	Molecule	
	Mirror plane (Å)	General position (Å)
C ₁ —C ₂	1.48 ± 0.04	1.49 ± 0.03
C ₂ —C ₃	1.31 ± 0.04	1.31 ± 0.03
C ₃ —C ₁	1.62 ± 0.04	1.51 ± 0.03
C ₄ —N	1.34 ± 0.04	1.39 ± 0.03
N—C ₁	1.60 ± 0.03	1.55 ± 0.02
N—O ₁	1.33 ± 0.03	1.32 ± 0.02
C ₂ —C ₅	1.57 ± 0.03	1.55 ± 0.02
C ₅ —O ₂	1.27 ± 0.03	1.24 ± 0.02
C ₅ —O ₃	1.22 ± 0.03	1.22 ± 0.02
O ₂ —K	2.64 ± 0.02	2.62 ± 0.02
C ₁ —C ₈	1.52 ± 0.03	1.63 ± 0.03
C ₁ —C ₉	1.52 ± 0.03	1.57 ± 0.03
C ₄ —C ₆	1.56 ± 0.03	1.55 ± 0.03
C ₄ —C ₇	1.56 ± 0.03	1.69 ± 0.03

* Nomenclature is explained in Fig. 3.

TABLE 4. *Intramolecular bond angles.**

Angle	Molecule	
	Mirror plane (degrees)	General position (degrees)
C ₁ —C ₂ —C ₃	114 ± 2	114 ± 2
C ₂ —C ₃ —C ₄	112 ± 2	112 ± 2
C ₃ —C ₄ —N	99 ± 2	102 ± 2
C ₄ —N—C ₁	118 ± 2	115 ± 2
N—C ₁ —C ₂	98 ± 2	98 ± 2
C ₁ —N—O ₁	117 ± 2	121 ± 2
C ₄ —N—O ₁	126 ± 2	124 ± 2
C ₁ —C ₂ —C ₅	125 ± 2	122 ± 2
C ₂ —C ₅ —O ₂	113 ± 2	116 ± 2
C ₂ —C ₅ —O ₃	118 ± 2	114 ± 2
C ₅ —O ₃ —K	179 ± 2	161 ± 2
C ₆ —C ₄ —C ₇	113 ± 2	116 ± 2
N—C ₄ —C ₆	111 ± 2	111 ± 2
N—C ₄ —C ₇	111 ± 2	103 ± 2
C ₈ —C ₁ —C ₉	114 ± 3	113 ± 2
N—C ₁ —C ₈	109 ± 2	107 ± 2
N—C ₁ —C ₉	109 ± 2	108 ± 2

* Nomenclature is explained in Fig. 3.

of these compounds and especially in spin-label experiments where the electron spin resonance spectra of these radicals are used as structural probes in the study of biomolecules.¹⁰⁻¹⁷ The structure of a similar compound with the nitroxide group in a six-membered ring has recently been reported by Bonneteau.¹⁸ In this compound the $\begin{matrix} \text{C} \\ \diagup \\ \text{N} \end{matrix}$ —O group is not planar, and the length of the three-electron N—O bond of 1.26 Å compares well with the 1.23 Å found by Hanson¹⁹ in di-p-anisyl nitric oxide (III). In HO—C₅H₄(CH₃)₄—NO(II) Bonneteau found chains of molecules with oxygen atoms associated with HO and NO groups, each 2.94 Å apart. This relatively close approach is interpreted as a hydrogen bond. Our results suggest that it must be a very weak hydrogen bond since only one of the two types of I in the unit cell forms a similar hydrogen bond on crystallization from aqueous medium.

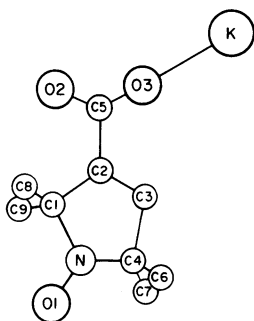


FIG. 3.—Line diagram of the molecule showing the nomenclature used in this paper.

The structure of I differs from that of II in some very interesting details. Two types of molecule with different geometries coexist in crystals of I—both are flat, but only one lies in a crystallographic mirror plane. The best plane through the five-membered ring, calculated by a method of least squares for molecules of the second type, is given by the equation

$$-0.6197u + 0.0491v + 0.7833w = -0.2875,$$

where u , v , and w are Ångstrom coordinates. The deviations of atoms from this plane are given in Table 2. Within experimental error this molecule is therefore also flat. The important molecular parameters of both types of molecule are listed in Tables 3, 4, and 5. Of particular interest are the distances between non-

TABLE 5. Distances between some nonbonded atoms.*

Approach	Molecule	
	Mirror plane (Å)	General position (Å)
N—C2	2.32 ± 0.03	2.29 ± 0.02
N—C3	2.26 ± 0.04	2.26 ± 0.03
C1—C3	2.34 ± 0.05	2.35 ± 0.03
C1—C4	2.51 ± 0.04	2.48 ± 0.03
C2—C4	2.43 ± 0.04	2.34 ± 0.03
C6—C7	2.61 ± 0.04	2.67 ± 0.03
C8—C9	2.56 ± 0.04	2.75 ± 0.04
O1—C6	3.00 ± 0.04	3.02 ± 0.03
O1—C7	3.00 ± 0.04	3.06 ± 0.03
O1—C8	3.02 ± 0.03	2.94 ± 0.04
O1—C9	3.02 ± 0.03	3.00 ± 0.04
O1—O(H ₂ O)	2.84 ± 0.04	—
K—O3	2.64 ± 0.02	2.62 ± 0.02
K—O2	2.82 ± 0.03	2.61 ± 0.02
O(H ₂ O)—K	3.92 ± 0.04	2.83 ± 0.02

* Nomenclature is explained in Fig. 3.

bonded atoms, which dramatically illustrate the steric protection of the free methyl groups. The average C(methyl)—O distance in this region is 3.01 Å, which indicates a clustering of atoms.

At this stage of refinement it appears that, apart from the differences in planarity of the $\begin{matrix} \text{C} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{C} \end{matrix}$ —O grouping, the N—O bond is significantly longer (1.34 Å average) in I than in either II (1.26 Å) or III (1.23 Å). This lengthening cannot be explained by possible hydrogen bonding, which occurs only with the molecule in the mirror plane and does not seem to play a similar role in the structure of II. Furthermore, the N—C(4) bond in I has the length of a typical double bond, and if both of the crystallographically distinct molecules in the unit cell had not exhibited the same effect, we would have been tempted to ascribe its occurrence to systematic errors. However, a discussion of these effects must await more detailed refinement of the structure.

¹ Rozantzev, E. G., and L. A. Krinitzkaya, *Tetrahedron*, **21**, 491 (1965).

² Buerger, M. J., *Crystal-Structure Analysis* (New York: John Wiley and Sons, Inc., 1960), p. 61.

³ *Ibid.*, p. 86.

⁴ This program, written in Fortran for the IBM 360/40H by E. G. Boonstra, corrects for *Lp*, spot shape, absorption, and α_1 - α_2 splitting.

⁵ All Fourier summations were carried out with suitable computer programs written by Gantzel and Hope at UCLA and obtained through the courtesy of Dr. M. J. Laing of the University of Natal, Durban. Suitable modifications to allow their use on the IBM 360/40H were made by Miss J. Hewitt.

⁶ *International Tables for X-ray Crystallography* (Birmingham: Kynoch Press, 1952), vol. 1, p. 117.

⁷ Hamilton, W. C., *Acta Cryst.*, **8**, 185 (1955).

⁸ The least-squares program ORFLS of Martin, Busing, and Levy as well as their function and error program ORFFE were modified for use on our computer by H. Messerschmidt of IBM (SA).

⁹ Atomic scattering factors were obtained from Hanson, H. P., F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

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- ¹⁸ Lajzerowicz-Bonneteau, J., *Acta Cryst.*, B24, 196 (1968).
- ¹⁹ Hanson, A. W., *Acta Cryst.*, 6, 32 (1953).