CRYSTAL STRUCTURE OF THE POTASSIUM SALT OF 2-METHYL-5-DINITROMETHYLTETRAZOLE

E. A. Goiko, N. V. Grigor'eva, G. V. Makarenko,
N. V. Margolis,* A. A. Mel'nikov, T. K. Strochkina,
and I. V. Tselinskii

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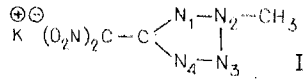
In a continuation of a study of the structure and reactivity of the anions of dinitromethyl compounds [1, 2] and in an attempt to clarify the structure of tetrazole derivatives, we synthesized the potassium salt of 2-methyl-5-dinitromethyltetrazole (and carried out its complete x-ray diffraction crystallographic analysis.



I

5-Dinitromethyltetrazole salts substituted at a tetrazole ring nitrogen atom have not yet been reported in the literature.

N-Methyl-5-chlorodinitromethyltetrazole was obtained by the alkylation of 5-chlorodinitromethyltetrazole by dimethyl sulfate in 65% aqueous ethanol with subsequent treatment with ethanolic KOH, which led to the formation of potassium salt I.

The structure of I might have been either the 1- or 2-alkyl-substituted isomer [3]. Thin-layer chromatography and PMR spectroscopy indicated the isolation of only one isomer. Analysis of the work of Fokin et al. [3] indicated the probable formation of the N_2 isomer.† The x-ray diffraction analysis confirmed this hypothesis. There are two crystallographically independent anions in the crystal of I which differ in structure but are N_2 isomers. I crystallize as elongated, transparent, light yellow platelets which are stable in the air and light and resistant to change in temperature and x-ray radiation.

Monoclinic crystals of I have the following unit cell parameters: a = 26.26(5), b = 8.16(2), c = 15.36(5) Å, β = 96° ± 40', V^3 = 1638 Å^3, d = 1.84 ± 0.02 g/cm^3, Z = 16.

The space group could not be determined unequivocally from the extinctions. Either Cc or C2/c were possible. Diffraction patterns were obtained using copper radiation and a Weissenberg equiinclination diffractometer for hk0—hk9. A total of 1455 nonzero reflections were recorded. The integral intensities of these reflections were determined photometrically. Weak reflections were determined visually. The F^2 (hk$l$) values were obtained by introducing LP factors. The structure was solved by the heavy atom method. The position of the potassium ions and dinitromethyl groups were determined in the Cc space group. These are pairwise related by symmetry centers. This showed that the crystal has a centrosymmetric space group. Then, three consecutive electron density maps were carried out in space group C2/c. The tetrazole ring and methyl group carbon atoms were found from these maps.

Finally, the structure was refined by the method of least squares using the Rentgen-75 program [4] on a BESM-6 computer. The final R value was 0.08 (for 1348 reflections).

Table 1 gives the relative coordinates of the nonhydrogen atoms and their isotropic temperature factors.

Analysis of the structure showed that there are crystallographically independent anions differing in structure in the independent part of the unit cell. The configurations of these anions are shown in Fig. 1a, b. The bond lengths and angles are also given. The error in

*Deceased.

†We did not adopt the number of the nitrogen atoms according to Benson. The N_2 isomer has substitution at N_5 and N_{11}.

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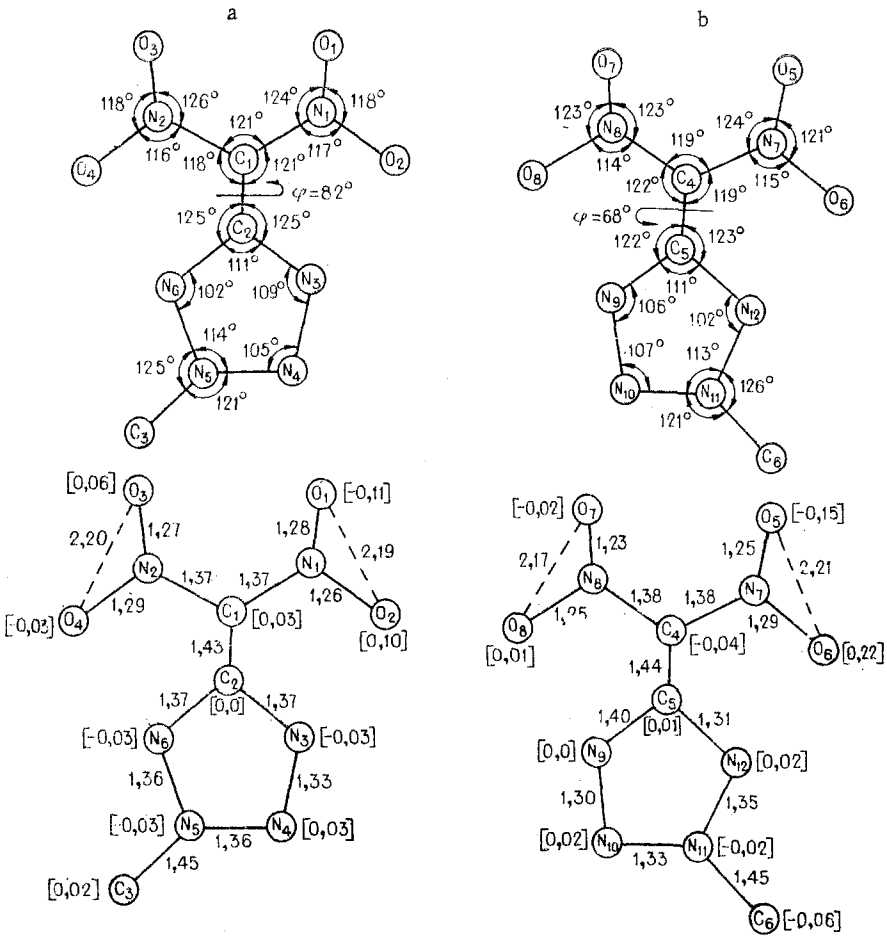

Fig. 1. Configuration of the anions [a) anion A, b) anion B] in the structure of the potassium salt of 2-methyl-5-dinitromethyltetrazole. The deviations of the nitro group atoms from the planes of the $C_2C_1N_1N_2$ and $C_5C_4N_7N_8$ planes (in Å) are given in brackets. The deviations of the ring atoms from the planes of the $C_1C_2N_3N_4N_5N_6$ and $C_4C_5N_9N_{10}N_{11}N_{12}$ tetrazole rings are also given in brackets.

TABLE 1. Relative Coordinates of the Atoms and Their Isotropic Temperature Factors

Atom	x	y	z	U_i	Atom	x	y	z	U_i
K_1	0.0733	0.0224	0.2714	2.32	N_5	0.3624	0.0362	0.7471	2.18
K_2	0.1551	0.1503	0.0338	3.00	N_6	0.3158	0.9725	0.7541	2.44
O_1	0.1660	0.1078	0.8575	3.40	N_7	0.5139	0.3069	0.4252	1.89
O_2	0.2450	0.1386	0.9146	3.96	N_8	0.5176	0.3063	0.5825	2.12
O_3	0.1521	0.0942	0.6870	2.06	N_9	0.4331	0.0393	0.4677	2.75
O_4	0.2221	0.0736	0.6246	3.68	N_{10}	0.3848	0.0062	0.4753	3.23
O_5	0.5600	0.3516	0.4253	2.96	N_{11}	0.3653	0.1429	0.5061	2.89
O_6	0.4858	0.2954	0.3554	3.41	N_{12}	0.3995	0.2652	0.5194	2.51
O_7	0.5615	0.3617	0.5929	3.14	C_1	0.2318	0.1040	0.7694	1.88
O_8	0.4944	0.2710	0.6482	3.21	C_2	0.2870	0.1029	0.7641	1.84
N_1	0.2131	0.1152	0.8484	2.54	C_3	0.4048	0.9439	0.7352	3.70
N_2	0.2000	0.0918	0.6910	2.06	C_4	0.4920	0.2734	0.5013	1.84
N_3	0.3150	0.2439	0.7644	2.60	C_5	0.4410	0.1968	0.4957	2.00
N_4	0.3622	0.1981	0.7530	2.87	C_6	0.3115	0.1502	0.5254	3.11

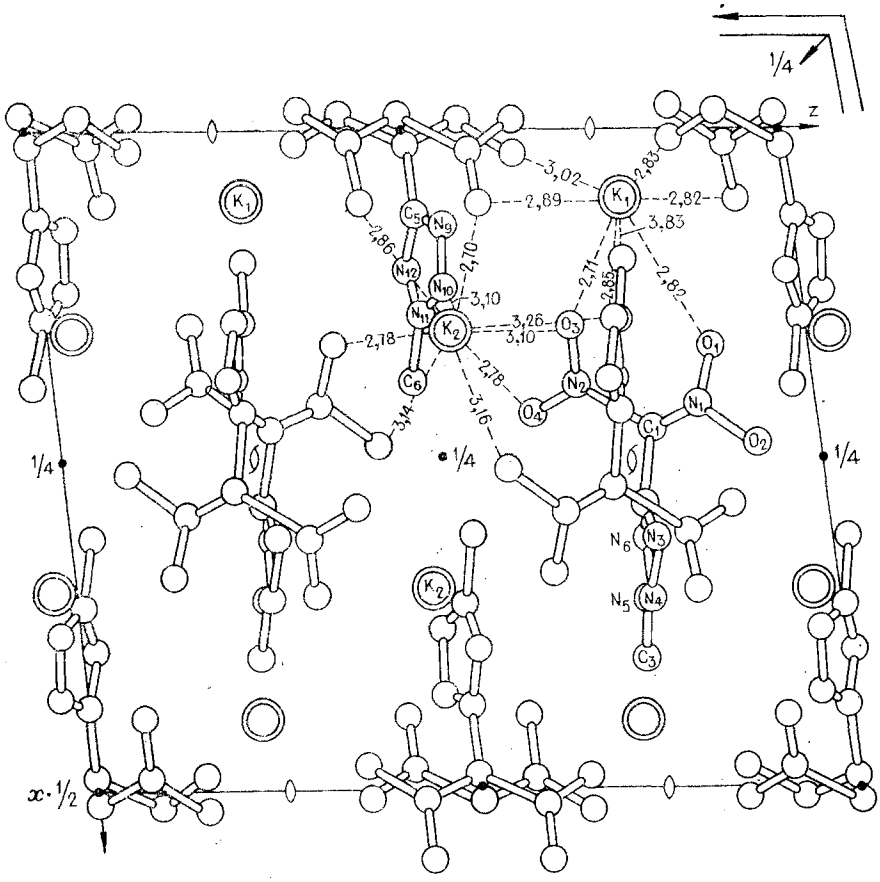

Fig. 2. Projection of the structure of the potassium salt of 2-methyl-5-dinitromethyltetrazole on the x/2z plane.

the bond lengths does not exceed 0.02 Å and the error in the bond angles does not exceed 2° (99% confidence level). The dinitromethyl fragment $C_2C_1N_1N_2$ is planar. The nitro groups are twisted about the C_1N_i bonds in anion A by 6° and 2° and by 8° and 0° in anion B. The planes of the $C_2N_3N_4N_5N_6$ and $C_5N_9N_{10}N_{11}N_{12}$ are twisted relative to the plane of the dinitromethyl group about the C_1—C_2 and C_4—C_5 bonds by 82° and 68°, respectively. This finding indicates a low energy barrier for rotation of the rings about the C—C bond. We may expect a continuous spectrum of rotational angles from 68° to 82° in solution. The projection of the structure of I onto the x/2z plane is shown in Fig. 2 along with the distances of the potassium ion from the nearest anion atoms. Potassium is hexacoordinated. The K—O distance is 2.70 Å. We should also note the somewhat shortened K_1—N_4 distance (2.85 Å), which indirectly indicates excess charge on N_4.

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