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THE CRYSTAL STRUCTURE OF DIPOTASSIUM TETRANITROETHIDE

by

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CHAPTER 1

Introduction

A carbanion may be thought of as being the heterolytic cleavage of a bond to a tetrahedrally substituted carbon atom when the bonding electron pair remains with the carbon atom. If the three remaining bonds to the carbon atom keep their original configurations, the carbanion will have a pyramidal structure. However, with substituent groups on the carbon atom such as nitro, cyano, or carbonyl, the negatively charged carbon atom can interact through resonance with these groups resulting in a net increase of the double bond character between the group and the carbon atom. This increase in double bond character will be accompanied by an increase in planarity of the structure from the original pyramidal configuration.

The currently available theories and knowledge about chemical bonding are not in an advanced enough state of development to allow the prediction of the exact geometry of a carbanion. Indeed there are only a few carbanions whose structures have been investigated and determined. Moreover it is possible that the configuration of a carbanion may vary according to the chemical environment of the ion, but this has not been sufficiently investigated. In many chemical reactions a carbanion intermediate is formed (1). Carbanion structural determinations are contributing to the understanding of these reactions and to the advancement of our knowledge about the nature of chemical bonding.

In a previous investigation Desiderato and Sass(2) have shown that the tricyanomethide carbanion is significantly non-planar in the crystalline ammonium salt despite the possibility of contributions to the anion structure by the canonical forms I, II, and III. Bugg and Sass(3) have also found a similar non-planarity in the pyridinium dicyanomethylide molecule IV.

The present investigation was undertaken in order to determine the structure of a polynitro-substituted carbanion, since no previous structural determinations had been reported for molecules of this type. The trinitromethide anion V was initially selected for investigation because of its structural analogy to the tricyanomethide anion. Salts of the trinitromethide anion were found to be unstable at room temperature and difficulty was encountered in obtaining the experimental data at low temperatures. A nitro compound with a more stable anion was finally chosen for study. This compound was dipotassium tetranitroethide which contains the tetranitroethide dianion VI.

I

II

III

IV

V

VI

CHAPTER II

Preparation of Materials

Dipotassium Tetranitroethide was prepared by the reaction of tribromonitromethane with potassium iodide by the method of Hunter (4) according to the overall equation shown below:

Twenty-five g. of Br_3CNO_2 was slowly added to 18.8 g. of KI dissolved in 500 ml of 95% ethyl alcohol. Magnetic stirring of the reaction mixture was continued for 15 minutes after the addition was completed. The precipitate of potassium bromide and dipotassium tetranitroethide which formed during the reaction was filtered off and washed with 95% ethyl alcohol. Saturated aqueous solutions of the product mixture were cooled from 80°C to 5°C to remove the potassium bromide. Two of these recrystallizations were necessary for complete purification. Well formed rhombohedral single crystals of dipotassium tetranitroethide were obtained by leaving loosely covered beakers of a saturated solution prepared from the salt and water at room temperature in a refrigerator until the crystals formed.

Determination of Cell Constants, Space Group, and Multiplicity

Crystals with a diameter of about 0.2 mm. were selected as specimens for X-ray diffraction analysis and mounted on glass fibers.

Rotation photographs showed the c rotation axis to be coincident with the needle axis of the crystal and the b rotation axis to be perpendicular to the needle axis and passing through the shorter

edge diagonal of the needle. Weissenberg and rotation photographs showed the dipotassium tetranitroethide crystals to be monoclinic with cell constants of $a=13.027 \pm 0.020 \text{ \AA}$, $b=7.556 \pm 0.017 \text{ \AA}$, $c=13.546 \pm 0.023 \text{ \AA}$, and $\beta=140.87^\circ$. All reflections with $h+k=2n+1$ were absent, indicating a c centered unit cell. Systematic absences were also observed for $h0\ell$ reflections with $\ell=2n+1$. These systematic absences are caused by a c glide-plane perpendicular to the b axis. The centrosymmetric space group $C2/c-C_{2h}^6$ and the noncentro-symmetric space group $Cc-C_s^4$ are the only monoclinic space groups containing symmetry elements consistent with the above absences. These space groups cannot be distinguished from each other by systematic absences.

The density of dipotassium tetranitroethide was experimentally determined to be 2.24 g./cc. by the flotation method using a mixture of CH_2Br_2 and CCl_4 . The theoretical density of the crystalline material is 0.58 g./cc. for each molecule of compound contained in the unit cell which indicates that the multiplicity value is 4.

Collection of Reflection Intensities

Integrated intensities for 600 independent reflections were recorded on films using a Nonius integrating Weissenberg camera and filtered $\text{CuK}\alpha$ radiation. Weissenberg data were obtained around the b rotation axis for $k = 0-4$ and around the c rotation axis for $\ell = 0-6$. All photographs were recorded simultaneously on three superimposed films. The integrated intensity values were measured with a Welch Densichron Densitometer. Corrections were applied for the Lorentz, polarization, and Tunnell effects (5,p. 152). No corrections were made for absorption and extinction.

CHAPTER III

Solution of the Two-dimensional Trial Structure

Since the b axis was about twice as short as the a and c axes it was thought that the best opportunity for obtaining a two-dimensional solution of the crystal structure would be with the [010] projection. Accordingly the Patterson projection $P(u,w)$ shown in figure 1 was synthesized using the relative intensities of the observed $h0\ell$ reflections.

The two-dimensional solution of the structure was initiated by assuming that the correct space group was $C2/c$ whose [010] projection is shown in figure 2. There is an eightfold multiplicity in the general positions of this space group. Each tetranitroethide ion in a unit cell must thus be across a two-fold axis or a center of symmetry to yield the experimentally observed multiplicity of four molecules per unit cell. Therefore, the asymmetric unit contains only one-half of one molecule.

A set of x and z trial parameters for the potassium atom was obtained from the two-dimensional Patterson synthesis. All the vectors between atoms in the unit cell of a compound are represented in a Patterson map as vectors from the map origin to peaks in the map. Each peak's height is proportional to the product of the atomic numbers of the two atoms whose interatomic vector is being mapped. Thus the highest peaks in a Patterson projection for dipotassium tetranitroethide should be due to potassium-potassium interactions or to the accidental superposition of several weaker peaks from other types of interactions.

Figure 1 - $P(u, w)$

There must be one potassium ion located at each of the eight general positions of the space group C2/c which are shown below:

$$x, y, z$$

$$\bar{x}, \bar{y}, \bar{z}$$

$$\bar{x}, y, 1/2 - z$$

$$x, \bar{y}, 1/2 + z$$

$$1/2 + x, 1/2 + y, z$$

$$1/2 - x, 1/2 - y, \bar{z}$$

$$1/2 + x, 1/2 - y, 1/2 + z$$

$$1/2 - x, 1/2 + y, 1/2 - z$$

The potassium ions will interact to produce Patterson peaks at the following positions in the three-dimensional vector map:

Type	u	v	w
I	$\pm 2x$	$\pm 2y$	$\pm 2z$
II	$\pm 2x$	$\mp 2y$	$\pm 2z$
III	$1/2 \pm 2x$	$1/2 \pm 2y$	$\pm 2z$
IV	$1/2 \pm 2x$	$1/2 \mp 2y$	$\pm 2z$
V	$\pm 2x$	0	$1/2 \pm 2z$
VI	$1/2 \pm 2x$	$1/2$	$1/2 \pm 2z$
VII	$1/2$	$1/2 \pm 2y$	$1/2$
VIII	0	$\pm 2y$	$1/2$
IX	$1/2$	$1/2$	0

In the two-dimensional Patterson projection down the b axis the only heavy-atom peaks which need to be considered in determining the

heavy-atom x and z parameters are types I, II, V, and VI because each of the other types is either coincident with one of these types in projection or is in a special position which provides no information about x and z parameters. The b Patterson projection for dipotassium tetranitroethide contains two large unique peaks of about equal height with coordinates of $u = 0.250$, $w=0.250$, and $u=0.250$, $w=0.100$. No satisfactory x and z trial parameters for potassium could be obtained using the former peak. If the latter peak is assumed to be a heavy-atom peak of type I, the parameters for the potassium ion may be calculated to be $x=0.125$ and $z=0.05$. A one-atom trial structure using these parameters gives an R value of 58%. Calculations based upon the assumption of one of the other heavy-atom peak types will only shift one or both of the above potassium parameters by 0.25. This is equivalent to keeping the parameters constant and shifting the origin in the [010] electron density projection by the same amount. Two-dimensional structures differing only by such an origin shift are indistinguishable for the space group $C2/c$.

The [010] superposition projection was calculated via the d_{gen} synthesis (6) using the potassium parameters previously obtained and the relative intensities of the observed $h0l$ reflections. A search was made around the centers of symmetry and twofold axes of the superposition projection for an image of a planar tetranitroethide ion with its plane parallel to the projection plane. This was done by centering a scaled drawing of the ion on each unique center and twofold axis of the superposition and rotating the drawing to determine if all its

Figure 3 - [010] Superposition Projection

atoms could be made to coincide with peaks in the superposition. Figure 3 shows the two-dimensional superposition along with the best fitting tetranitroethide image that could be located. The positions of the peaks in this image were used to calculate the x and z parameters for a two-dimensional trial structure. A least-squares refinement of these parameters reduced the R of the trial structure from an initial value of 39% to final value of 16%.

Solution of the Three-dimensional Trial Structure

Two sets of three-dimensional trial parameters for the potassium ion were calculated from the parameters of the three-dimensional Patterson heavy-atom peaks in the following table:

Peak	u	v	w
— 1	0.000	0.183	0.500
2	0.000	0.817	0.500
3	0.750	0.183	0.600
4	0.750	0.817	0.600

These calculations were done assuming peaks 1 and 2 to be of type VIII and peaks 3 and 4 to be of type I. The sets of calculated parameters for the heavy atom are shown below:

Set	x	y	z
A	0.375	± 0.092	0.300
B	0.375	± 0.408	0.300

The choice of sign of the heavy-atom y parameter determines the direction of the positive b axis in the coordinate system and does not contribute any additional ambiguity to the result. Thus the solution of a Patterson function for a crystal of space group $C2/c$ for the coordinates of an atom in a general position contains an inherent twofold ambiguity. This ambiguity can only be resolved by testing the related trial structures for agreement with the experimental data.

In the two-dimensional structure the tetranitroethide anion was centered on the center of symmetry projection located at $x=0.250$ and $z=0.000$ and the coordinates for the potassium ion were $x=0.125$ and $z=0.050$. Comparison of the two- and three-dimensional cation coordinates showed that the former needed to be translated by 0.250 in x and 0.250 in z to become equivalent with the latter. Accordingly all the refined two-dimensional coordinates were subjected to the above transformation to yield the x and z parameters for the three-dimensional trial structure. This translation moved the center of the anion from a center of symmetry to a twofold rotation axis.

The anion y parameters for the three-dimensional trial structure were obtained from packing considerations and the knowledge that the anion must possess a twofold rotation axis. Set A proved to be the correct coordinates for the potassium ion.

The Structure Refinement

A three-dimensional isotropic least-squares refinement was used

TABLE 2

Final Atomic Parameters for $K_2C_2N_4O_8$

Atom	X	Y	Z	B
C2	0.5621 ± 0.0014	0.5459 ± 0.0016	0.3335 ± 0.0013	0.45 ± 0.19
O1	0.4144 ± 0.0013	0.7313 ± 0.0014	0.3173 ± 0.0012	1.62 ± 0.19
O2	0.6274 ± 0.0014	0.6177 ± 0.0018	0.5431 ± 0.0014	2.67 ± 0.24
O3	0.7322 ± 0.0011	0.4054 ± 0.0015	0.3553 ± 0.0011	1.33 ± 0.17
O4	0.8270 ± 0.0012	0.4750 ± 0.0015	0.3701 ± 0.0012	1.49 ± 0.18
N1	0.5371 ± 0.0013	0.6359 ± 0.0015	0.4042 ± 0.0013	0.82 ± 0.19
N2	0.7098 ± 0.0013	0.4692 ± 0.0015	0.4216 ± 0.0012	0.51 ± 0.17
K	0.3725 ± 0.0003	0.0999 ± 0.0005	0.3012 ± 0.0004	0.96 ± 0.07

to reduce the R of the trial structure from 43% to 12.3%. The calculation was done with an IBM 7094 computer using the least-squares analysis program ORFLS written by Busing and Levy (7). In this refinement the atomic parameters X_i were adjusted to minimize the function

$$\sum_j \left[\sqrt{w_j} \left(F_j^{\text{obs}} - F_j^{\text{calc}} \right) - \sqrt{w_j} \sum_i \left(\frac{\partial F_j^{\text{calc}}}{\partial X_i} \right) \Delta X_i \right]^2$$

Unobserved reflections were omitted from the refinement. During the latter stages of the least-squares analysis the original unit weighting scheme was abandoned in favor of a modified Hughes weighting scheme (8). With this scheme w was set equal to $1/F^2$ for all F 's larger than $4F_{\text{min}}$. For all other F 's, a w of $16F_{\text{min}}^2/F^4$ was used. Table 1 shows the agreement between the observed and calculated structure factors upon the completion of the isotropic refinement. Table 2 gives the final atomic parameters obtained by the refinement and their estimated standard deviations.

TABLE 1

Calculated and Observed Structure Factors for $K_2C_2N_4O_8$

H	L	F _{obs}	F _{calc}	H	L	F _{obs}	F _{calc}
K=0				K=0			
2	0	-59.84	-47.58	-8	6	44.27	42.51
4	0	-123.51	-118.22	-10	6	109.26	103.41
6	0	-28.91	-24.76	-12	6	-33.49	-13.29
8	0	44.14	42.75	-14	6	-23.44	-18.94
0	2	-69.99	-63.21	0	8	-92.02	-114.53
2	2	-77.82	-74.72	-4	8	-130.56	135.53
4	2	24.13	31.39	-6	8	24.48	37.79
6	2	142.41	145.46	-10	8	-48.13	-38.47
8	2	-30.20	-38.85	-12	8	105.29	92.15
-2	2	-34.80	-20.84	0	10	27.22	46.25
-4	2	131.37	155.52	-2	10	55.31	47.19
-6	2	-125.13	-134.46	-4	10	-84.66	-102.44
-8	2	-64.00	-60.97	-6	10	60.93	60.20
-10	2	34.04	31.76	-8	10	92.14	83.88
0	4	-71.83	-62.38	-12	10	-95.65	-81.93
2	4	121.73	138.87	-14	10	-32.33	-25.91
4	4	-79.61	-78.29	-16	10	18.62	17.44
-2	4	-183.79	-187.14	-2	12	54.97	56.88
-4	4	-120.17	-101.41	-4	12	26.93	38.99
-6	4	91.31	87.06	-6	12	40.45	-48.96
-8	4	46.12	43.85	-8	12	-160.99	-153.90
-10	4	-21.18	-28.29	-10	12	49.16	36.38
-12	4	-30.81	-30.40	-12	12	32.97	28.82
0	6	24.49	21.71	-16	12	-59.97	-43.84
2	6	-64.95	-75.10	-6	14	49.51	45.92
4	6	-46.43	-41.22	-10	14	-86.04	-70.67
-2	6	200.43	191.65	-12	14	32.40	19.20
-4	6	-25.12	-24.84	-14	14	83.86	70.28
-6	6	-253.18	-252.01	-16	14	20.64	13.64

TABLE 1

H	K=0	L	F _{obs}	F _{calc}	H	K=1	L	F _{obs}	F _{calc}
-8		16	30.48	44.57	-9		3	37.96	40.94
-10		16	<u>35.31</u>	46.02	-11		3	34.61	42.06
-14		16	-60.48	-56.14	1		4	-131.75	-138.83
	K=1				3		4	-59.57	-57.09
1		0	33.23	26.99	5		4	51.88	46.18
3		0	100.13	101.83	7		4	28.77	34.78
5		0	53.11	56.71	-1		4	96.98	82.02
7		0	-88.09	-97.51	-3		4	121.53	123.30
3		1	-26.12	-27.51	-5		4	-125.88	-161.97
5		1	-28.53	-24.33	-9		4	38.49	41.46
7		1	34.86	46.56	-11		4	27.48	26.59
9		1	50.07	52.21	-13		4	-17.48	-22.93
-3		1	-143.16	-188.85	1		5	62.60	62.80
-5		1	30.46	21.82	5		5	-44.05	-51.38
-7		1	51.28	49.25	-3		5	-17.41	-10.26
-11		1	-37.97	-44.11	-5		5	52.22	55.51
1		2	143.33	171.60	-7		5	56.39	54.83
3		2	-37.82	-43.14	-9		5	-54.09	-56.19
-1		2	-42.96	-41.62	-13		5	34.69	35.31
-3		2	-67.60	-91.56	3		6	22.15	37.88
-5		2	-130.01	-138.88	5		6	-19.54	-33.21
-7		2	81.00	90.41	-3		6	-58.90	-49.36
-9		2	28.00	22.23	-5		6	71.20	69.13
-11		2	-60.55	-63.36	-9		6	-88.04	-84.72
3		3	-33.65	-29.91	-13		6	77.32	76.01
3		3	-33.65	-29.91	3		7	-26.96	-26.31
5		3	32.32	39.53	-1		7	64.77	60.40
7		3	-21.44	-20.67	-3		7	-18.97	-9.83
-1		3	-58.70	-51.71	-5		7	-20.12	-17.97
-5		3	-55.36	-55.10	-7		7	48.17	40.74

TABLE 1

H	K=1	L	F _{obs}	F _{calc}	H	K=1	L	F _{obs}	F _{calc}
-9		7	97.86	90.83	-15		12	88.08	78.01
-11		7	-39.61	-37.17	-7		13	-25.21	-22.20
-13		7	-72.93	-59.62	-9		13	42.89	38.60
3		8	-36.18	-44.84	-11		13	66.46	56.02
-1		8	46.03	51.43	-13		13	-39.40	-29.74
-5		8	-74.35	-73.34	-15		13	-29.34	-24.28
-7		8	67.38	56.69	-7		14	-63.22	-69.86
-9		8	62.19	56.64	-9		14	71.29	74.28
-11		8	49.18	46.90	-15		14	-28.98	-26.09
-13		8	-55.00	-51.43	-13		15	55.92	48.31
-3		9	25.42	26.08	-9		16	-33.37	-31.71
-7		9	-70.75	-62.17	-11		16	-30.28	-25.49
-15		9	-51.29	-43.48	-13		16	64.08	62.90
-1		10	-21.66	-25.01	-13		17	-26.76	-27.36
-3		10	57.99	65.86		K=2			
-5		10	84.47	85.69	0		0	137.17	171.16
-7		10	-59.74	-58.74	2		0	-101.34	-108.20
-9		10	-91.86	-71.03	6		0	33.53	31.14
-11		10	121.83	104.51	10		0	-14.18	-8.26
-13		10	-51.91	-46.49	0		1	-117.26	-145.44
-15		10	-48.48	-39.71	2		1	-57.95	-53.45
-5		11	-45.57	-47.35	4		1	133.57	137.43
-7		11	35.06	22.88	-2		1	-103.87	-131.06
-9		11	-25.63	-27.71	-4		1	84.28	85.83
-11		11	-48.59	-39.24	-6		1	-27.78	-28.60
-15		11	66.93	58.17	-8		1	-73.13	-72.50
-3		12	-33.11	-51.53	-10		1	21.59	29.66
-5		12	31.77	30.18	0		2	49.96	45.25
-7		12	-22.24	-23.60	2		2	42.96	30.79
-11		12	-75.07	-71.17	6		2	41.73	44.64

TABLE 1

H	K=2	L	F _{obs}	F _{calc}	H	K=2	L	F _{obs}	F _{calc}
8		2	-32.80	-38.10	2		6	23.26	20.06
-2		2	-124.72	-132.16	-2		6	46.55	39.68
-4		2	21.37	26.39	-6		6	-74.54	-62.13
-6		2	-65.16	-61.61	-8		6	47.21	44.12
-10		2	48.40	46.89	-12		6	-31.34	-28.69
0		3	96.65	88.12	-14		6	-16.54	-17.94
2		3	71.00	61.34	2		7	35.10	45.62
4		3	-85.81	-79.51	4		7	20.37	32.00
6		3	-70.80	-67.11	-2		7	-42.04	-38.95
-2		3	-235.47	-240.79	-4		7	45.23	45.65
-4		3	-54.18	-57.94	-6		7	119.72	108.56
-6		3	79.69	85.81	-8		7	-36.35	-22.75
-8		3	93.43	91.68	-10		7	-48.06	-40.44
-10		3	-54.78	-63.05	-14		7	30.86	29.29
-12		3	-21.38	-16.42	0		8	-40.27	-33.27
0		4	-24.39	-25.83	2		8	21.93	25.70
2		4	43.63	39.46	-4		8	-26.27	-30.32
4		4	-76.45	-75.62	-6		8	-49.06	-47.50
-4		4	104.95	115.66	-12		8	69.59	43.24
-6		4	25.04	20.60	0		9	72.68	87.84
-10		4	-21.39	-28.02	-4		9	-78.62	-75.01
0		5	19.57	11.55	-6		9	-68.61	-61.39
2		5	-53.06	-56.24	-8		9	126.05	113.31
4		5	-36.99	-36.29	-10		9	-37.76	-33.55
6		5	25.65	41.72	-12		9	-92.31	-77.04
-2		5	186.92	166.54	-14		9	-46.71	-34.26
-4		5	71.20	-52.63	-2		10	32.88	32.99
-6		5	-80.89	-80.84	-4		10	-32.46	-26.81
-8		5	52.24	48.88	-6		10	52.85	51.60
-10		5	80.24	78.68	-10		10	-39.75	-32.53
0		6	-39.61	-31.80	-12		10	-43.25	-36.88

TABLE 1

H	K=2	L	F _{obs}	F _{calc}	H	K=3	L	F _{obs}	F _{calc}
-2		11	24.91	33.79	-1		2	-49.33	-50.63
-6		11	-73.46	-68.54	-3		2	43.00	45.41
-8		11	-84.12	-90.44	-9		2	37.73	41.75
-10		11	32.38	25.65	1		3	-96.47	-81.56
-12		11	93.27	75.78	3		3	-106.81	-105.46
-14		11	-57.82	-46.47	5		3	66.26	66.86
-8		12	-36.82	-26.38	-3		3	132.40	131.59
-10		12	21.72	26.94	-5		3	15.82	20.26
-16		12	-26.00	-19.15	-7		3	-60.34	-57.19
-4		13	-46.30	-45.81	-11		3	28.45	34.08
-6		13	49.01	65.21	1		4	27.81	28.44
-12		13	-27.34	-16.09	-3		4	49.58	42.47
-14		13	69.20	58.19	-5		4	45.34	49.14
-16		13	22.91	28.43	-7		4	71.30	75.86
-14		14	41.17	31.42	-9		4	-19.41	-28.49
-16		14	-24.38	-24.62	-11		4	-43.08	-43.14
-14		15	-51.50	-47.44	1		5	105.40	103.37
-12		16	-20.40	-20.26	3		5	34.65	41.66
-14	K=3	16	-32.92	-33.09	5		5	-36.69	-36.89
1		0	-33.44	-37.57	-1		5	-97.68	-97.48
5		0	-13.14	-12.25	-3		5	-121.95	-109.37
7		0	-20.56	-11.42	-5		5	63.83	72.92
9		0	28.51	22.39	-7		5	108.41	110.62
1		1	120.27	106.62	-9		5	-49.40	-52.39
-3		1	-228.61	-259.79	-13		5	23.06	30.25
-5		1	-43.95	-34.58	1		6	30.09	23.22
-7		1	54.80	53.82	-1		6	44.88	41.33
-9		1	35.63	36.36	-5		6	-47.15	-45.42
1		2	-72.06	-60.74	-7		6	35.55	37.95
5		2	34.62	30.38	-9		6	-57.06	-48.04
7		2	-31.01	-33.80	3		7	-46.74	-48.55

TABLE 1

H	K=3	L	F _{obs}	F _{calc}	H	K=3	L	F _{obs}	F _{calc}
-1		7	109.77	110.04	-15		13	-36.44	-26.34
-5		7	-97.94	-98.76	-9		14	26.30	29.11
-7		7	-48.53	-34.52	-15		14	21.64	15.70
-9		7	141.59	129.57	-13		15	56.14	43.35
-13		7	-56.24	-48.43	-9		15	-31.69	-30.00
-3		8	-57.98	-58.09	-11		16	-41.93	-37.62
-9		8	-89.63	-66.29	-13		16	-24.71	-19.95
-11		8	53.54	43.33	K=4				
1		9	-17.62	-27.05	0		0	-81.70	-90.08
-1		9	-45.36	-52.99	8		0	-79.42	-84.47
-3		9	83.51	84.00	4		0	54.66	51.62
-5		9	68.98	73.19	0		1	-43.13	-40.49
-7		9	-64.99	-54.39	2		1	-25.79	-24.31
-9		9	-65.31	-57.57	4		1	81.69	76.00
-13		9	34.03	26.78	-2		1	-23.02	-26.56
-15		9	-48.81	-45.12	-4		1	52.93	56.97
-3		10	-46.80	-43.05	-8		1	-27.02	-33.76
-5		10	32.56	20.43	-10		1	47.69	46.70
-13		10	-34.63	-30.29	0		2	48.53	42.81
-15		10	42.77	37.20	4		2	-67.90	-68.22
-3		11	-33.21	-49.25	6		2	-25.32	-21.40
-5		11	-76.45	-85.03	8		2	15.54	29.24
-7		11	69.90	76.52	-2		2	-101.00	-125.90
-11		11	-40.72	-36.42	-4		2	28.81	34.65
-13		11	-34.51	-30.24	-6		2	86.97	89.18
-15		11	62.53	61.54	-8		2	28.20	24.75
-7		12	-26.29	-32.47	0		3	63.61	53.14
-9		12	41.33	36.20	4		3	-41.23	-35.30
-5		13	-25.27	-27.25	6		3	-32.86	-38.20
-7		13	-62.02	-62.57	-2		3	-51.18	-51.66
-11		13	106.01	92.91	-4		3	37.88	48.59

TABLE 1

H	K=4	L	F _{obs}	F _{calc}	H	K=4	L	F _{obs}	F _{calc}
-6		3	29.25	31.42	-14		9	-22.84	-19.95
-8		3	27.28	26.55	0		10	-20.26	-36.54
-10		3	-45.14	-48.69	-8		10	-27.39	-23.64
6		4	25.72	30.98	-10		10	35.58	22.55
-4		4	99.65	118.01	-12		10	57.00	47.93
-6		4	75.35	-67.97	-2		11	16.08	24.42
-8		4	33.55	32.91	-8		11	-51.47	-44.77
-10		4	44.19	41.60	-12		11	72.44	58.38
-2		5	74.69	64.80	-14		11	52.87	-38.28
-4		5	-43.88	-38.68	-4		12	31.58	31.52
-6		5	-79.51	-83.93	-6		12	42.02	40.78
-10		5	35.46	31.60	-8		12	42.00	43.05
-12		5	-22.31	-17.13	-14		12	64.00	53.75
0		6	-31.23	-22.14	-6		13	36.65	49.18
2		6	102.21	111.11	-14		13	32.33	24.33
-2		6	23.68	20.47	-10		14	65.57	61.63
-4		6	49.98	41.94	-12		14	21.08	17.44
-6		6	32.09	31.51	-10		15	25.06	32.68
-8		6	60.28	-53.41	-12		15	-30.13	-44.61
-10		6	-99.70	91.23	K=5				
-12		6	24.60	27.62	1		0	53.56	46.82
0		7	46.60	-39.04	3		0	-49.58	38.70
-6		7	23.42	21.36	5		0	-65.07	63.53
-12		7	51.75	39.28	7		0	34.61	31.47
-2		8	29.72	33.90	1		1	-78.96	-74.74
-4		8	113.21	-107.41	5		1	35.19	35.64
-8		8	52.06	50.24	-1		1	32.17	39.77
-12		8	-85.47	-71.11	-5		1	54.30	39.90
0		9	24.22	28.95	-7		1	37.80	27.40
-8		9	70.75	72.95	1		2	-139.45	-146.55
-10		9	-43.57	40.10	3		2	22.92	32.45

TABLE 1

H	K=5	L	F _{obs}	F _{calc}	H	K=6	L	F _{obs}	F _{calc}
5		2	58.74	59.09	-6		1	31.47	37.63
7		2	-20.03	-21.07	-8		1	36.76	30.05
-3		2	85.68	97.93	0		2	77.89	83.59
-5		2	50.83	50.24	2		2	46.20	50.25
-7		2	-77.28	-81.77	4		2	-40.80	-35.08
1		3	24.38	28.19	6		2	-18.58	-25.51
5		3	29.12	24.80	-2		2	-61.78	-71.91
-1		3	35.13	40.52	-4		2	-54.65	-50.86
1		4	93.56	90.71	-6		2	33.40	30.60
3		4	26.49	28.26	2		3	-35.77	-28.74
5		4	-28.96	-32.97	4		3	34.47	40.81
-1		4	-70.12	-67.93	-2		3	54.58	66.08
-3		4	-66.51	-73.89	-4		3	45.53	59.99
-5		4	49.64	54.18	-6		3	-30.48	-46.05
-7		4	94.43	92.67	2		4	-51.60	-52.99
-9		4	-28.95	-32.94	-2		4	32.14	32.96
-11		4	-51.82	-61.07	-4		4	52.97	58.60
1		5	53.27	43.13	-6		4	-85.63	-96.54
-7		5	-88.36	-79.30	2		5	36.02	40.50
-9		5	-32.02	-33.18	4		5	19.91	22.94
-1		6	74.73	68.33	-2		5	-38.13	-37.21
-3		6	58.27	46.81	-6		5	-32.50	-34.78
-5		6	-104.29	-107.77	-10		5	-42.11	-52.34
-11		6	21.13	25.42	0		5	-50.73	-60.01
K=6					2		6	51.87	58.91
0		0	-96.32	-85.95	-2		6	-54.83	-58.59
4		0	60.02	57.90	-6		6	65.77	62.53
6		0	32.03	28.38	-10		6	-37.64	042.83
8		0	-48.25	-53.11	K=7				
4		1	-27.97	-29.54	7		7	25.99	25.72

TABLE 1

H	K=7	L	F _{obs}	F _{calc}	H	K=8	L	F _{obs}	F _{calc}
1		1	-74.93	-80.40	0		3	-40.99	-47.89
3		1	29.77	26.24	2		3	-59.33	-69.23
5		1	60.55	70.10	-2		3	47.43	61.21
-3		1	50.58	44.81	-4		3	41.92	54.38
-7		1	-35.97	-29.67	-6		3	-24.85	-37.72
3		2	26.92	23.78	-2		4	-33.91	-34.34
5		2	16.21	18.87	-4		4	-26.25	-32.23
-7		2	-31.34	-36.21	-2		5	-69.78	-74.70
1		3	29.10	33.15	-4		5	27.56	29.48
-1		3	23.49	31.97	-6		5	14.70	25.04
-3		3	-54.36	-65.42	K=9				
-5		3	61.38	69.69	1		0	-28.40	-25.75
-7		3	33.84	31.66	3		0	23.03	23.52
-9		4	-17.95	-16.76	1		1	-49.64	-52.76
-1		5	32.83	29.39	-1		1	-27.28	-16.44
-5		5	-26.38	-26.80	1		2	29.81	38.96
-9		5	47.37	52.92	-3		3	-51.42	-70.01
1		6	-26.47	-26.63	-5		3	21.99	32.81
-5		6	-26.82	-24.59	-1		4	17.32	27.47
-7		6	38.05	31.50	-5		4	-30.98	-45.05
-9		6	24.64	26.19	-3		5	16.63	16.87
K=8					-5		6	25.40	42.61
0		0	45.53	47.56	-8		5	-30.27	-32.38
4		0	-30.21	-22.54					
0		1	47.51	40.72					
2		1	25.49	30.49					
4		1	-44.97	-47.62					
-2		1	-30.99	-30.56					
-4		1	-85.97	-73.90					
-6		1	17.52	14.41					
-4		2	22.34	17.60					

CHAPTER IV

Discussion

Figure 4 shows the [010] projection of the crystal structure of dipotassium tetranitroethide. The interatomic distances and angles in the tetranitroethide dianion are given in table 3. In nitromethane the C-N and N-O bond lengths are 1.46 and 1.21 Å respectively (10). Thus there is a lengthening of the N-O bond and a shortening of the C-N bond in the tetranitroethide ion. These changes may be attributed to resonance

interactions of the type $R_2C=N^+ \begin{array}{l} \diagup O^- \\ \diagdown O^- \end{array}$. The C1-C2 bond distance is

intermediate between the normal C-C single bond value of 1.54 Å and the normal double bond value of 1.34 (9, p. 228). Part of the decrease in the C-C bond length may be attributed to a factor other than an increased multiple-bond character. According to Coulson (14), a bond formed with sp^2 orbitals will be shorter than a bond formed with sp^3 orbitals because the orbital overlap is intensified by the increased s character.

Within experimental error the O-N-O bond angles are in agreement with the value of 121° found in dipotassium nitroacetate (11). The O1-N1-O2 and O3-N2-O4 planes make angles of 13.0° and 6.3° with the N1-C2-N2 plane respectively. There is an angle of 63.1° between the N1-C2-N2 and N3-C1-N4 planes. This twist of the nitrogen atoms about

TABLE 3

Interatomic Dimensions in $K_2C_2N_4O_8$

Distance		Angle	
C1-C2	$1.43 \pm 0.02 \text{ \AA}$	01-N1-O2	$121.08 \pm 2^\circ$
C2-N1	$1.40 \pm 0.02 \text{ \AA}$		
C2-N2	$1.38 \pm 0.02 \text{ \AA}$	03-N2-O4	$119.49 \pm 2^\circ$
N1-O1	$1.24 \pm 0.02 \text{ \AA}$		
N1-O2	$1.23 \pm 0.02 \text{ \AA}$	01-N1-C2	$116.36 \pm 2^\circ$
N2-O3	$1.24 \pm 0.02 \text{ \AA}$		
N2-O4	$1.27 \pm 0.02 \text{ \AA}$	03-N2-C2	$119.49 \pm 2^\circ$
N1-N2	$2.43 \pm 0.02 \text{ \AA}$		
N2-N4	$3.06 \pm 0.02 \text{ \AA}$	02-N1-C2	$122.52 \pm 2^\circ$
N1-N3	$3.06 \pm 0.02 \text{ \AA}$		
O1-O2	$2.15 \pm 0.02 \text{ \AA}$	04-N2-C2	$120.81 \pm 2^\circ$
O3-O4	$2.17 \pm 0.02 \text{ \AA}$		
O1-O6	$2.87 \pm 0.02 \text{ \AA}$	N1-C2-N2	$121.33 \pm 2^\circ$
O3-O8	$2.87 \pm 0.02 \text{ \AA}$		
O1-O3	$4.49 \pm 0.02 \text{ \AA}$	N1-C2-C1	$120.09 \pm 2^\circ$
O1-O4	$3.98 \pm 0.02 \text{ \AA}$		
O2-O3	$4.04 \pm 0.02 \text{ \AA}$	N2-C2-C1	$118.35 \pm 2^\circ$
O2-O4	$2.57 \pm 0.02 \text{ \AA}$		

the C1-C2 molecular axis was indicated in the trial structure to increase the intermolecular atomic distances across the centers of symmetry in the crystal lattice.

Atom N1 is 0.017 Å° above the O1-C2-O2 plane while N2 is 0.035 Å° below the O3-C2-O4 plane. The carbon atom C2 is 0.040 Å° below the plane of its substituents N1, N2 and C1 which is a planar configuration within the limits of the experimental error and indicates that most of the negative charge of the anion is located on the oxygen atoms.

The variations in the configurations of the two nitro groups may be due to forces in the crystal lattice since each of the nitro-group oxygens is in a different chemical environment in the lattice. Each oxygen atom has two potassium ions as its nearest intermolecular atomic neighbors with corresponding O-K distances of 2.81 and 2.87 Å° for O1, 2.79 and 3.00 Å° for O2, 2.68 and 2.85 Å° for O3, and 2.76 and 2.84 Å° for O4. The shortest O-O intermolecular distance is 3.09 Å° across a center of symmetry. The shortest K-C approach is 4.00 Å° which further confirms that most of the negative charge on the anion is distributed on the oxygen atoms. The minimum O-K distance of 2.68 Å° is consistent with the values of 2.73 Å° in potassium paranitrophenyldicyanomethide (12), 2.70 Å° in dipotassium nitroacetate (11), and 2.68 Å° in potassium bicarbonate (13).

Several additional refinement operations should be executed before this study is considered complete. An anisotropic least squares refinement is needed. This should not change the present atomic coordinates significantly but it might correct the unsatisfactory thermal vibration

Figure 4 - [010] Projection of $\text{K}_2\text{C}_2\text{N}_4\text{O}_8$

parameters, lower the R of the structure, and improve the accuracy of the molecular parameters. The refinements should also be attempted with the non-centric space group for a final verification that the assumption of a centrosymmetric crystal structure is correct. These calculations are being postponed until more precise diffraction data can be collected by using an automatic single crystal X-ray diffractometer so that the final results will be as accurate as can be obtained with currently available X-ray diffraction equipment.

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