ACTA CHEMICA SCANDINAVICA 26 (1972) 1921–1930

Refinement of the Crystal Structure of Potassium Cyanodinitromethanide

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The crystals are orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 6.82_9$ Å, $b = 12.26_6$ Å, and $c = 6.64_1$ Å. 1288 X-ray reflections were recorded as observed on an automatic four-circle diffractometer. Those having $\sin\theta/\lambda > 0.50$ Å^{-1}, in all 926, were used in the full-matrix least squares refinement ($R_w = 4.5$ %, $R = 4.9$ %). The central carbon atom and its neighbours are coplanar. The anion is propeller shaped with the nitro groups twisted 7° from a planar conformation and has C_2 symmetry.

Crystal structure studies of potassium cyanodinitromethanide were undertaken in this laboratory and independently by Dr. James R. Holden, but as we had progressed further with the data collection, his work was discontinued. The rubidium salt was also investigated. Three-dimensional diffractometer data were collected when papers by Grigor' eva *et al.* on these compounds appeared.[1–3] The accuracy of their determinations was rather low, however, and refinement based on the diffractometer data was therefore carried out.

The refinement of the crystal structure of rubidium cyanodinitromethanide has been published,[4] and references to other studies of dinitrocarbanions may be found in Ref. 5. In order to study the variations in anion parameters when nitro groups are replaced by cyano groups, crystal structure determinations of dicyanonitromethanide salts are also planned in this laboratory.

EXPERIMENTAL

Potassium cyanodinitromethanide was synthesized as described by Parker *et al.*[6] Crystals suitable for X-ray studies were obtained by recrystallization from aqueous solution. The space group is $P2_12_12_1$. The cell dimensions and estimated standard deviations were determined at room temperature on a manual four-circle diffractometer using CuK radiation.

1470 reflections with $2\theta < 72°$ were measured on an automatic four-circle diffractometer. Mo$K\alpha$ radiation (0.002″ Nb filter) and $\omega/2\theta$ scan technique were applied. A crystal of length 0.39 mm mounted with $\mathbf{a}^* + \mathbf{c}^*$ along the φ axis of the diffractometer was used for all X-ray work. The shape of the crystal could be described by eight planes and the

cross section was approximately 0.28×0.34 mm^2. The low angle data ($2\theta < 53°$) consisting of 738 reflections were registered previous to the high angle data. The standard reflections were quite stable during the data collection, the decrease in intensities being 4 % or less. 1288 reflections were regarded as observed having intensities greater than twice their standard deviations estimated from counting statistics. (158 of the 182 unobserved reflections belonged to the high angle data.) The standard reflections were used for scaling and a 2 % uncertainty in scaling and diffractometer stability were included in the standard deviations.

The data were corrected for absorption. The transmission factor varied from 0.77 to 0.81.

All computer programs used are described in Ref. 7.

The atomic form factors of Cromer and Waber [8] were applied and the anomalous scattering factor values for potassium ($\Delta f' = 0.235$ and $\Delta f'' = 0.254$) have been calculated by Cromer and Liberman.[9]

CRYSTAL DATA

Potassium cyanodinitromethanide, $KC_2N_3O_4$, *F.W.* 169.1. Slightly yellow plates or diamond shaped prisms, orthorhombic. $a = 6.829(1)$, $b = 12.266(2)$, $c = 6.641(1)$ Å, $V = 556.3$ Å^3. $F(000) = 332$, $Z = 4$; $\varrho_{obs} = 1.99$ g cm^{-3}, $\varrho_{calc} = 2.019$ g cm^{-3}; $\mu = 0.90$ mm^{-1}. Space group $P2_12_12_1$.

STRUCTURE REFINEMENT

The atomic parameters determined earlier from three-dimensional film data by the heavy atom method were used as starting parameters in the full-matrix least squares refinement which converged at an R_w of 8.8 % for all reflections. When the strongest reflections (about 120) were omitted from the refinement an R_w of 7.3 % was obtained. The conventional R for all reflections decreased from 6.5 % to 5.5 %, indicating that systematical experimental errors might be present as well as extinction effects. Refinement including all reflections corrected for secondary extinction gave $R_w = 6.9$ % ($R = 5.3$ %). By successively increasing the lower limit of $\sin\theta/\lambda$ for the reflections used in the least squares calculations, R_w was lowered while R for all reflections remained fairly constant. Only the 926 observed intensities having $\sin\theta/\lambda > 0.50$ Å^{-1} were included in the final refinement cycles. Introduction of anomalous scattering factor for potassium resulted in an R_w-value of 4.49 % ($R_w = 4.75$ % for the other enantiomer). The corresponding R-factors were 4.8 % and 5.5 % for the 926 and all observed reflections, respectively. The weight analysis based on the standard deviations in intensities showed negligible intensity dependence except for the smallest F-values.

Observed and calculated structure factors and final atomic parameters with estimated standard deviations are listed in Table 1 and Table 2, respectively. An analysis of the atomic vibration tensors is presented in Table 3. The r.m.s. discrepancy between atomic vibration components derived from the thermal parameters of Table 3 and those calculated from a rigid-body model [10] is 0.0021 Å^2, thus indicating a fairly rigid anion. The reduced r.m.s. translational amplitudes are 0.159, 0.149, and 0.134 Å. The r.m.s. librational amplitudes are 5.8, 3.8, and 3.3°. The axis of largest libration is nearly parallel to the axis having the least moment of inertia, the N1···N2 direction.

Table 1. Observed and calculated structure factors. (The five columns list values of h, k, l, $10\,F_o$, and $10\,F_c$.)

h	k	l	Fo	Fc
0	4	0	1315	1310
0	6	0	173	167
0	8	0	239	215
0	10	0	250	232
0	12	0	178	162
0	14	0	166	153
0	16	0	42	36
0	18	0	58	56
1	1	0	58	58
1	2	0	368	337
1	3	0	249	215
1	4	0	422	338
1	5	0	571	563
1	6	0	54	68
1	7	0	92	89
1	8	0	109	105
1	9	0	297	298
1	10	0	18	6
1	11	0	81	80
1	13	0	93	95
1	15	0	28	29
1	16	0	35	39
1	17	0	23	25
2	0	0	180	171
2	1	0	297	274
2	2	0	285	282
2	3	0	232	217
2	4	0	590	558
2	5	0	52	42
2	6	0	253	238
2	7	0	284	278
2	8	0	370	349
2	9	0	14	17
2	10	0	43	20
2	11	0	154	156
2	12	0	83	78
2	13	0	27	23
2	14	0	55	51
2	15	0	33	30
2	16	0	84	87
2	18	0	49	55
2	19	0	21	14
3	1	0	339	337
3	2	0	320	326
3	3	0	155	196
3	4	0	231	231
3	5	0	130	126
3	6	0	235	229
3	7	0	75	66
3	8	0	61	62
3	9	0	214	210
3	10	0	57	53
3	11	0	30	29
3	12	0	46	42
3	13	0	114	111
3	14	0	45	49
3	18	0	37	37
3	19	0	23	11
4	0	0	426	443
4	1	0	45	31
4	2	0	180	182
4	3	0	264	262
4	4	0	248	242
4	5	0	27	13
4	6	0	77	85
4	7	0	131	125
4	8	0	95	92
4	9	0	42	41
4	12	0	57	57
4	13	0	50	47
4	15	0	22	25
4	17	0	29	28
5	1	0	11	19
5	2	0	205	203
5	3	0	67	73
5	4	0	81	84
5	5	0	145	147
5	6	0	63	67
5	7	0	132	136
5	8	0	51	55
5	9	0	92	90
5	10	0	129	133
5	11	0	47	52
5	12	0	26	29
5	13	0	49	48
5	14	0	59	63
5	16	0	27	18
5	17	0	41	41
6	0	0	144	129
6	1	0	80	75
6	2	0	116	117
6	3	0	88	93
6	4	0	116	109
6	5	0	96	95
6	6	0	45	42
6	7	0	57	57
6	8	0	90	86
6	9	0	16	13
6	10	0	42	43
6	12	0	60	58
6	16	0	32	31
7	1	0	159	159
7	2	0	119	118
7	3	0	45	42
7	4	0	107	110
7	5	0	149	150
7	6	0	231	233
7	8	0	71	72
7	9	0	88	89
7	10	0	112	116
7	11	0	21	18
7	12	0	32	35
7	13	0	44	44
7	14	0	41	47
8	0	0	189	191
8	1	0	131	133
8	2	0	42	41
8	3	0	119	117
8	4	0	149	147
8	5	0	26	26
8	7	0	47	52
8	8	0	57	56
8	9	0	19	14
8	11	0	32	34
8	13	0	30	30
9	1	0	41	38
9	2	0	143	142
9	4	0	21	24
9	6	0	85	84
9	8	0	37	46
9	9	0	45	39
9	10	0	86	83
9	11	0	54	52
10	0	0	20	19
10	1	0	41	42
10	2	0	31	34
10	3	0	67	69
10	5	0	64	63
10	6	0	42	42
10	7	0	65	66
11	2	0	70	69
0	1	1	43	41
0	2	1	356	316
0	3	1	303	271
0	4	1	828	789
0	5	1	297	255
0	6	1	33	12
0	7	1	37	22
0	8	1	37	16
0	9	1	121	95
0	10	1	62	57
0	11	1	53	47
0	12	1	37	37
0	13	1	43	41
0	15	1	57	56
0	18	1	26	18
0	19	1	33	37
1	0	1	13	13
1	1	1	415	351
1	2	1	791	687
1	3	1	355	318
1	4	1	488	440
1	5	1	222	213
1	6	1	490	459
1	7	1	309	291
1	8	1	214	195
1	9	1	78	73
1	10	1	256	246
1	11	1	85	86
1	12	1	102	103
1	13	1	42	38
1	14	1	106	106
1	15	1	16	24
1	16	1	43	44
1	17	1	26	30
1	18	1	35	41
2	0	1	194	174
2	1	1	452	426
2	2	1	529	485
2	3	1	573	547
2	4	1	216	207
2	5	1	76	62
2	6	1	108	94
2	7	1	295	285
2	8	1	138	121
2	9	1	63	58
2	10	1	24	23
2	11	1	137	135
2	12	1	36	27
2	13	1	40	29
2	14	1	20	19
2	15	1	48	45
2	16	1	53	56
2	17	1	34	30
3	0	1	344	330
3	1	1	251	272
3	2	1	529	541
3	3	1	237	238
3	4	1	38	23
3	5	1	111	110
3	6	1	356	350
3	7	1	35	18
3	8	1	64	89
3	9	1	66	99
3	10	1	175	171
3	11	1	83	75
3	12	1	77	75
3	13	1	69	71
3	14	1	99	98
3	15	1	45	45
3	16	1	37	40
3	17	1	23	26
3	18	1	48	45
3	19	1	27	20
4	0	1	140	149
4	1	1	156	164
4	2	1	83	86
4	3	1	231	227
4	4	1	206	221
4	5	1	169	182
4	6	1	106	115
4	7	1	270	270
4	8	1	150	151
4	9	1	78	83
4	10	1	29	33
4	11	1	140	139
4	12	1	87	89
4	13	1	41	45
4	14	1	21	19
4	15	1	66	66
4	16	1	44	46
4	18	1	22	28
5	0	1	38	39
5	1	1	106	100
5	2	1	371	368
5	3	1	118	110
5	4	1	22	21
5	5	1	120	117
5	6	1	176	179
5	7	1	47	47
5	8	1	51	53
5	9	1	96	95
5	10	1	90	89
5	12	1	48	49
5	13	1	34	36
5	14	1	43	40
6	0	1	408	420
6	1	1	113	116
6	2	1	189	188
6	3	1	153	159
6	4	1	303	310
6	5	1	68	69
6	6	1	202	202
6	7	1	108	107
6	8	1	157	158
6	9	1	39	45
6	10	1	93	95
6	11	1	70	67
6	12	1	68	68
6	13	1	21	25
6	14	1	60	60
6	15	1	31	28
7	0	1	103	108
7	1	1	85	84
7	2	1	93	92
7	3	1	29	28
7	4	1	50	49
7	5	1	96	96
7	6	1	72	69
7	7	1	62	61
7	8	1	40	39
7	9	1	65	66
7	10	1	65	64
7	11	1	34	31
7	13	1	38	37
7	14	1	37	38
8	0	1	121	122
8	1	1	28	27
8	2	1	20	20
8	3	1	68	68
8	4	1	128	129
8	5	1	32	34
8	6	1	45	44
8	7	1	19	14
8	8	1	109	109
8	9	1	28	29
8	10	1	22	20
8	12	1	68	69
8	13	1	26	24
9	0	1	51	49
9	1	1	44	44
9	2	1	50	49
9	3	1	47	46
9	4	1	50	47
9	5	1	58	55
9	6	1	43	42
9	7	1	41	42
9	8	1	26	32
9	9	1	41	42
9	10	1	42	46
9	11	1	38	36
10	0	1	89	90
10	1	1	31	31
10	2	1	42	37
10	3	1	26	25
10	4	1	78	78
10	5	1	33	28
10	6	1	35	34
10	7	1	19	20
10	8	1	55	53
11	1	1	49	50
0	0	2	239	240
0	1	2	429	400
0	2	2	289	267
0	3	2	124	103
0	4	2	785	722
0	5	2	45	42
0	6	2	321	309
0	7	2	80	4
0	8	2	516	502
0	9	2	15	20
0	10	2	134	135
0	11	2	44	13
0	12	2	110	109
0	13	2	55	52
0	14	2	54	51
0	15	2	23	17
0	16	2	54	49
0	18	2	22	8
1	0	2	148	119
1	1	2	498	452
1	2	2	535	474
1	3	2	517	466
1	4	2	94	51
1	5	2	158	150
1	6	2	169	151
1	7	2	268	251
1	8	2	255	259
1	9	2	115	110
1	10	2	32	24
1	11	2	60	45
1	12	2	85	86
1	13	2	90	88
1	14	2	25	21
1	15	2	32	25
1	16	2	27	30
1	17	2	53	50
1	19	2	23	19
2	0	2	706	656
2	1	2	133	112
2	2	2	225	210
2	3	2	260	244
2	4	2	365	322
2	5	2	67	72
2	6	2	155	147
2	7	2	128	120
2	8	2	247	233
2	9	2	108	107
2	10	2	93	89
2	11	2	27	25
2	12	2	237	236
2	13	2	22	22
2	14	2	35	32
2	15	2	46	47
2	16	2	80	83
3	0	2	512	485
3	1	2	197	194
3	2	2	102	88
3	3	2	217	216
3	4	2	314	294
3	5	2	305	291
3	6	2	80	79
3	7	2	175	168
3	8	2	142	142
3	9	2	78	71
3	10	2	118	119
3	11	2	67	65
3	12	2	49	49
3	13	2	37	36
3	14	2	79	80
3	15	2	54	52
3	16	2	38	38
3	17	2	43	45
3	18	2	27	31
4	0	2	116	107
4	1	2	232	242
4	2	2	102	103
4	3	2	114	116
4	4	2	193	206
4	5	2	164	163
4	6	2	98	98
4	7	2	117	114
4	8	2	186	191
4	9	2	106	106
4	10	2	102	103
4	11	2	105	106
4	12	2	88	90
4	13	2	31	27
4	14	2	20	22
4	16	2	33	30
5	0	2	239	259
5	1	2	164	170
5	2	2	242	269
5	3	2	202	215
5	4	2	184	198
5	6	2	219	243
5	7	2	49	65
5	8	2	88	94
5	9	2	39	39
5	10	2	58	58
5	11	2	42	47
5	12	2	66	65
5	13	2	63	64
5	14	2	25	29
5	15	2	19	19
5	16	2	34	36
5	17	2	33	38
6	0	2	93	98
6	1	2	85	87
6	2	2	130	132
6	3	2	40	35
6	4	2	136	137
6	5	2	18	22
6	6	2	91	89
6	7	2	45	46
6	8	2	116	116
6	9	2	67	72
6	11	2	30	35
6	12	2	68	68
6	13	2	21	21
6	14	2	21	23
6	15	2	38	37
6	16	2	27	36
7	0	2	30	23
7	1	2	98	98
7	2	2	187	186
7	3	2	116	117
7	4	2	40	41
7	5	2	83	85
7	6	2	68	69
7	7	2	93	93
7	9	2	43	46
7	10	2	83	84
7	11	2	42	36
7	14	2	51	55
8	0	2	50	49
8	1	2	74	72
8	2	2	59	57
8	3	2	115	115
8	4	2	40	39
8	5	2	37	34
8	6	2	27	27
8	7	2	110	113
8	8	2	51	49
8	9	2	25	23
8	10	2	43	42
8	11	2	52	53
8	12	2	49	46
8	13	2	27	30
9	0	2	35	35
9	1	2	33	32
9	2	2	130	132
9	3	2	38	33
9	4	2	26	28
9	6	2	124	125
9	7	2	61	55
9	10	2	52	55
9	11	2	27	24
10	1	2	54	50
10	2	2	21	23
10	3	2	43	42
10	5	2	26	26
10	6	2	41	39
10	7	2	38	37
0	1	3	218	194
0	2	3	361	321
0	3	3	351	337
0	4	3	287	283
0	5	3	46	26
0	6	3	323	314
0	7	3	117	113
0	8	3	14	2
0	9	3	118	109
0	10	3	130	131
0	11	3	112	117

Table 1. Continued.

h	k	l	F_o	F_c
0	13	3	42	36
0	14	3	65	63
0	15	3	75	81
0	17	3	24	22
0	18	3	32	30
0	19	3	28	33
1	0	3	390	366
1	1	3	361	349
1	2	3	534	491
1	3	3	327	305
1	4	3	60	52
1	5	3	170	166
1	6	3	320	297
1	7	3	132	131
1	8	3	91	87
1	9	3	63	53
1	10	3	155	146
1	11	3	135	136
1	12	3	92	92
1	13	3	39	38
1	14	3	77	74
1	15	3	39	39
1	16	3	32	28
1	17	3	22	24
1	18	3	26	31
2	0	3	394	342
2	1	3	195	189
2	2	3	164	155
2	3	3	206	202
2	4	3	238	213
2	5	3	302	289
2	6	3	125	127
2	7	3	246	246
2	8	3	108	106
2	9	3	54	48
2	10	3	139	140
2	11	3	86	84
2	12	3	32	32
2	13	3	50	50
2	14	3	71	72
2	15	3	32	27
2	16	3	30	24
2	18	3	20	16
3	0	3	346	325
3	1	3	29	22
3	2	3	234	223
3	3	3	57	56
3	4	3	316	300
3	5	3	236	228
3	6	3	229	218
3	7	3	61	66
3	8	3	131	126
3	9	3	160	157
3	10	3	205	198
3	11	3	89	87
3	12	3	25	25
3	13	3	22	23
3	14	3	95	100
3	15	3	23	27
3	16	3	25	19
3	18	3	26	30
4	0	3	217	216
4	1	3	230	224
4	2	3	79	82
4	3	3	144	140
4	4	3	181	186
4	5	3	115	112
4	6	3	103	95
4	7	3	76	72
4	8	3	121	116
4	9	3	65	56
4	10	3	131	129
4	11	3	43	42
4	12	3	70	67
4	13	3	34	30
4	14	3	70	76
4	15	3	60	61
4	16	3	30	33
5	0	3	57	62
5	1	3	166	164
5	2	3	141	151
5	3	3	44	48
5	4	3	110	115
5	5	3	85	87
5	6	3	203	208
5	7	3	64	66
5	8	3	113	113
5	9	3	35	33
5	10	3	120	120
5	11	3	36	39
5	12	3	34	36
5	13	3	55	57
5	14	3	35	34
5	16	3	26	21
5	17	3	21	24
6	0	3	132	148
6	1	3	89	95
6	2	3	23	22
6	3	3	41	39
6	4	3	174	185
6	5	3	117	122
6	6	3	143	145
6	7	3	40	57
6	8	3	109	117
6	9	3	36	36
6	10	3	88	92
6	11	3	29	28
6	12	3	32	38
6	13	3	21	17
6	14	3	30	31
6	15	3	22	18
7	0	3	89	88
7	1	3	139	139
7	2	3	45	44
7	3	3	129	133
7	4	3	36	35
7	5	3	119	117
7	6	3	17	21
7	7	3	50	51
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7	12	3	28	24
7	13	3	28	31
7	14	3	43	42
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8	3	3	64	63
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8	8	3	82	82
8	9	3	29	30
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10	2	3	23	20
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10	6	3	22	21
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0	4	4	252	243
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0	8	4	103	98
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1	14	4	18	12
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2	4	4	207	199
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2	12	4	69	66
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6	8	4	18	19
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6	13	4	19	27
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6	15	4	29	33
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2	2	5	285	292
2	3	5	287	291
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2	6	5	273	273
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5	3	5	142	138
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5	7	5	149	144
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6	1	5	56	52
6	2	5	157	160
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6	8	5	48	45
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6	13	5	19	6
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7	2	5	22	21
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7	11	5	41	41
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9	1	5	79	77
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9	5	5	58	56
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2	4	6	86	91
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2	8	6	76	81
2	9	6	103	108
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2	12	6	55	54
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2	16	6	33	31
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3	12	6	47	49
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4	4	6	95	94
4	5	6	138	135
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4	11	6	44	57
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5	1	6	57	55
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5	5	6	18	14
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Table 1. Continued.

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6	2	6	61	62
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6	5	6	64	64
6	6	6	103	103
6	7	6	86	82
6	8	6	46	45
6	9	6	50	53
6	10	6	79	76
6	11	6	44	46
7	0	6	115	113
7	1	6	60	54
7	2	6	65	59
7	3	6	27	20
7	4	6	82	80
7	5	6	44	36
7	6	6	49	44
7	8	6	40	38
7	10	6	27	33
8	1	6	47	49
8	2	6	96	94
8	3	6	61	62
8	4	6	63	64
8	5	6	45	45
8	6	6	70	71
8	7	6	40	39
8	8	6	53	52
9	0	6	31	33
9	2	6	43	46
9	4	6	28	33
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0	2	7	115	113
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0	5	7	68	72
0	6	7	219	224
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0	12	7	22	23
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1	0	7	61	62
1	1	7	93	96
1	2	7	87	87
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1	4	7	95	94
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1	6	7	87	87
1	7	7	51	43
1	8	7	69	66
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2	1	7	71	72
2	2	7	222	230
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2	8	7	75	76
2	10	7	105	107
2	11	7	18	10
2	12	7	38	42
2	13	7	39	43
2	14	7	51	56
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3	1	7	103	108
3	2	7	44	47
3	3	7	130	134
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3	5	7	93	96
3	6	7	22	28
3	7	7	88	90
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3	9	7	82	85
3	10	7	28	27
3	11	7	47	48
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3	13	7	22	19
3	14	7	24	25
4	0	7	19	20
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4	3	7	47	49
4	4	7	34	35
4	6	7	116	116
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4	9	7	30	29
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4	12	7	20	18
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5	7	7	52	54
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5	12	7	25	26
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7	4	7	99	92
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8	4	7	22	20
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0	3	8	113	113
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0	9	8	40	35
0	10	8	41	48
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1	4	8	156	155
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1	8	8	143	144
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1	12	8	81	87
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2	2	8	46	44
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3	12	8	52	56
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7	4	8	70	65
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1	7	9	61	64
1	10	9	51	47
1	11	9	39	36
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2	3	9	29	23
2	5	9	20	18
2	6	9	124	124
2	7	9	53	50
2	8	9	39	38
2	9	9	36	34
2	10	9	53	50
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3	4	9	61	60
3	5	9	49	48
3	7	9	38	39
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4	2	9	77	74
4	3	9	20	9
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4	6	9	60	60
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6	2	9	37	44
6	3	9	41	42
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0	2	10	39	39
0	3	10	48	45
0	5	10	96	97
0	6	10	39	38
0	7	10	24	13
1	0	10	103	104
1	1	10	24	25
1	4	10	86	85
1	5	10	20	20
1	7	10	23	27
2	0	10	34	37
2	1	10	37	36
2	3	10	21	22
2	4	10	30	31
2	5	10	35	31
2	6	10	27	33
3	0	10	91	90
3	1	10	32	22
3	3	10	26	29
3	4	10	79	79
3	5	10	21	20
4	1	10	27	33
4	2	10	46	48

Table 2. Fractional atomic coordinates and thermal parameters ($\times 10^5$) with estimated standard deviations. The temperature factor is given by exp $-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$. For numbering of atoms, see Fig. 1.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K^+	22781	11792	2712	1136	566	1210	218	685	226
	9	6	10	12	4	12	10	15	11
O11	48406	45487	31314	1544	569	1245	−135	332	431
	39	23	37	40	15	37	44	68	41
O12	61632	38975	58385	980	830	1520	−250	−388	411
	30	33	42	33	22	42	48	59	54
O21	35844	32721	86099	1524	812	1275	−408	−739	627
	42	30	39	44	22	46	54	79	51
O22	6761	29645	74370	1209	550	1600	−500	385	35
	37	23	42	34	15	42	37	69	43
N1	47229	40687	47968	999	350	987	−72	86	46
	29	16	37	31	10	35	28	60	34
N2	23835	33111	72349	1085	350	1080	−166	−126	71
	34	18	32	37	10	35	37	63	31
N3	633	40302	28284	1686	1104	2163	−322	−2067	757
	59	50	64	57	41	82	86	122	85
C0	28483	37477	53496	867	396	998	−90	−404	213
	33	21	37	31	11	33	38	65	43
C3	13259	38763	39596	1118	538	1310	−181	−819	240
	39	31	46	41	19	47	52	75	55

Table 3. The root mean square amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (Å) and B-values (Å^2) along the principal axes given by the components of a unit vector in fractional coordinates ($\times 10^3$).

Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
	.216	3.69	50	72	52
K^+	.177	2.46	90	39	94
	.138	1.51	−104	0	106
	.218	3.75	−15	75	59
O11	.195	2.99	138	−3	49
	.149	1.76	46	33	−130
	.258	5.25	−21	78	40
O12	.180	2.57	39	24	−138
	.146	1.69	140	5	45
	.264	5.52	−46	72	51
O21	.186	2.75	126	34	−45
	.147	1.71	60	−16	134
	.219	3.79	73	−70	20
O22	.192	2.91	27	21	143
	.146	1.69	124	37	−43
	.165	2.16	−51	76	15
N1	.154	1.88	116	19	85
	.145	1.67	73	23	−124
	.174	2.40	−92	58	47
N2	.153	1.85	13	−27	141
	.150	1.78	114	50	22
	.308	7.47	−43	69	66
N3	.241	4.59	87	43	−92
	.140	1.54	109	−7	99
	.182	2.62	−43	68	69
C0	.152	1.83	90	44	−87
	.128	1.30	107	−9	103
	.214	3.61	−56	65	70
C3	.181	2.58	78	49	−90
	.135	1.45	111	−1	99

Table 4. Bond distances and angles of the anion. Distances in parentheses are corrected for libration.

Bond distances (Å)		Bond angles (°)	
N1 − O11	1.256 (1.261)	C0 − N1 − O11	115.1
N1 − O12	1.221 (1.227)	C0 − N1 − O12	123.0
N2 − O21	1.228 (1.233)	O11 − N1 − O12	121.9
N2 − O22	1.248 (1.253)	C0 − N2 − O21	121.9
C0 − N1	1.389 (1.394)	C0 − N2 − O22	116.0
C0 − N2	1.398 (1.404)	O21 − N2 − O22	122.0
C0 − C3	1.399 (1.407)	N1 − C0 − N2	123.7
C3 − N3	1.159 (1.162)	N1 − C0 − C3	118.6
		N2 − C0 − C3	117.7
		C0 − C3 − N3	177.0

Table 5. Coordination distances of the potassium ion.

Atom	Equiv. pos.	No.	(Å)
O11	$1-x,-\frac{1}{2}+y,\frac{1}{2}-z$	1	3.00
O11	$-\frac{1}{2}+x,\ \frac{1}{2}-y,\ -z$	2	2.95
O12		1	3.08
O12	$-\frac{1}{2}+x,\ \frac{1}{2}-y,1-z$	3	2.70
O21		3	2.71
O21	$x,\ y,-1+z$	4	2.93
O22		4	3.09
O22	$\frac{1}{2}+x,\ \frac{1}{2}-y,1-z$	5	2.97
N3	$\frac{1}{2}+x,\ \frac{1}{2}-y,-z$	6	2.81

The corrected as well as the uncorrected bond distances and bond angles are given in Table 4. The latter values are also given in Fig. 1. The estimated standard deviations calculated from the correlation matrix of the least squares refinement are 0.004 Å or less for all bond length values, and 0.5° and 0.25° or less for angles of 180° or 120°. The coordination of the cation is shown in Fig. 2, and the corresponding distances are presented in Table 5.

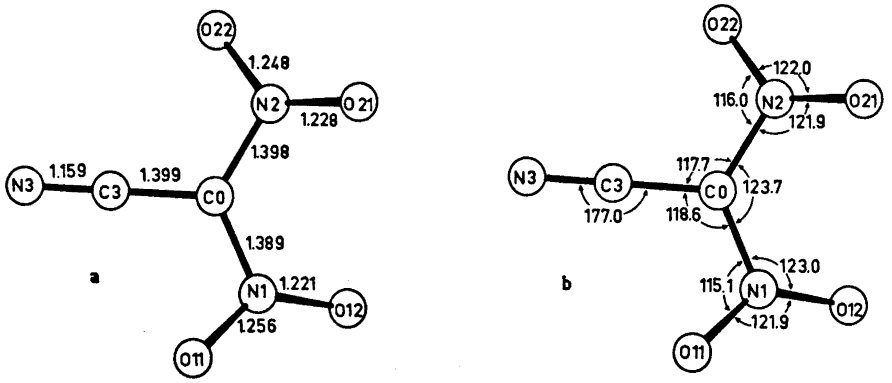

Fig. 1. (a) Bond distances (Å) and (b) bond angles (°) (uncorrected values) of the anion.

DISCUSSION

The anion is propeller shaped with the nitro groups twisted 7° from the planar conformation. In the corresponding rubidium salt [4] alternating twists of the nitro groups were observed. The effect of crystal forces on the conformation has also been demonstrated in the crystal structure determination of hydrazinium trinitromethanide [11] in which two independent anions are present.

The central carbon and its neighbour atoms are coplanar. The bend of the cyano group is illustrated by the deviations of N3 and C0 from the plane through N1, N2, and C1, 0.063 Å above and 0.005 Å below the plane, re-

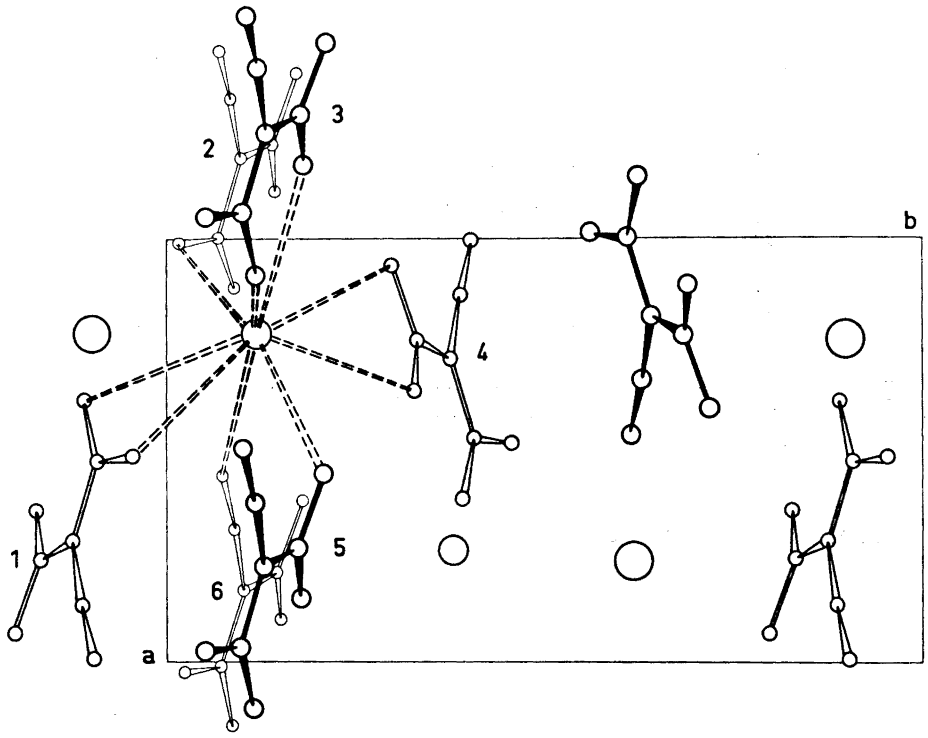

Fig. 2. A schematic drawing of the structure viewed along *c*. Equivalent position numbers of Table 5 are indicated.

spectively. The corresponding deviations of the oxygen atoms are 0.138 Å (O11), −0.124 Å (O12), 0.132 Å (O21), and −0.134 Å (O22). C0 is also coplanar with each of the nitro groups, which form angles of 7.0 and 7.1° with the least squares plane through C0, C1, N1, and N2.

The anion possesses non-crystallographic C_2 symmetry, as can be seen by inspection of bond distances and angles. Even the eigenvectors of the vibration tensors between "symmetry" related atoms (Table 3) are similar. Grigor'eva *et al.*[3] found the anion to be unsymmetrical. Their conclusions based on deviations from symmetry are incorrect according to the present findings.

The exclusion of low angle intensity data from the least squares refinements should greatly reduce any effects on the positional parameters caused by an asymmetry in the electron bonding density. (According to Allmann,[12] the contribution from the outer shell to the total scattering factor for carbon is less than 2 % at $\sin\theta/\lambda = 0.5$ Å^{-1}.) To illustrate the effect of asymmetry of the atomic charge distribution on the position of terminal atoms as determined with X-rays, Coppens and Coulson[13] have carried out approximate calculations with Slater orbitals for an oxygen atom in a nitro group. They

find that, depending on the hybridization, the centroid of the electron density on the oxygen atom usually is displaced outwards, away from the nitrogen atom, and that an increase of the ionic character in the N – O bond will reduce the asymmetry of charge. Similar unpublished calculations by Coppens (*cf.* Ref. 14) for the cyano group indicate a much smaller displacement of the nitrogen electronic charge center. In the present case the change in bond length caused by using the high angle data only in the refinement was by far most pronounced for the C3 – N3 bond; the lengthening being 0.013 Å (3σ). For the N – O bonds increases of 0.006 Å or less were obtained.

The bond angles of the anion do within the limits of error, agree with the findings for the rubidium compound. The C0 – C3 bond value of 1.399 Å (uncorrected) is the same as that found for the tricyanomethanide anion [15] (1.403 Å) and shows that the cyano group takes part in the charge delocalization. The C0 – N1 and C0 – N2 bonds (mean value 1.394 Å (uncorrected)) are normal; *cf.* Table 6 of Ref. 5 where data for several $RC(NO_2)_2^-$ anions are given. References and structural data for nitro compounds may also be found in a paper by Häfelinger,[16] where MO-π-bond order – bond length relations for π-systems with N – O bonds are derived.

In both nitro groups one N – O bond is found to be shorter than the other. Even though the bonds compared have one atom in common, the differences of 0.035 and 0.020 Å for the bond to N1 and N2, respectively, are quite large compared to the standard deviations in the bond lengths (0.0035 Å). As described below the two oxygen atoms forming the shorter bonds are coordinated to one potassium cation with $O\cdots K^+$ distances of 2.70 and 2.71 Å, whereas all other $O\cdots K^+$ distances are greater than 2.9 Å. One would rather expect a lengthening of the N – O bond, at least when π-electron densities are considered, if there was a strong interaction between an oxygen atom and a cation. The differences observed in the bond lengths may be due to differences in thermal motions. The three atoms making the shortest contacts to potassium (O12, O21, and N3) also exhibit the largest thermal vibration and have their major amplitudes roughly normal to the plane through the anion. The nitro groups have possibly a torsional motion about the bonds to the central carbon, and the rigid-body model [10] may not be the correct one. The application of the riding motion model [17] on the bonds to terminal atoms may also be questioned because of the coordination forces present as well as the assumption of this motion being linear. (The "riding" corrections were found to be 0.039 Å for C3 – N3, 0.023 Å for N1 – O12 and N2 – O21, and 0.015 Å for N1 – O11 and N2 – O22.) The O12···O21 contact is 2.66 Å.

The coordination about the potassium ion as shown in Fig. 2 is irregular and quite different from that of the rubidium salt. However, in both cases the cations are surrounded by eight oxygen atoms and one cyano nitrogen atom. As pointed out by Grigor'eva *et al.*[3] two oxygen atoms of one anion are located at a distance of about 2.70 Å from the cation whereas the other oxygen potassium contacts are well above 2.9 Å (Table 5). The nitrogen atom makes a short contact (2.81 Å) with another cation, and strongly bonded chains along [101] are formed. The nitrogen atom and potassium atom coordinated are situated at opposite sides of a least squares plane through the anion. The $C-N\cdots K^+$ angle is 165°, and the bending of the C – C≡N

angle, the value being 177°, is away from the potassium ion. The shortest *intra*-molecular distances are N···N (3.08 Å) and N···O (2.98 Å) between anions related by a screw axis along *c*, and N···O (2.97 Å) between anions related by a screw axis along *a*.

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Received October 21, 1971.