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Crystal Structures of Condensation Products of Malononitrile

I. The Potassium Salt of 2-Cyanomethyl-1,1,3,3-tetracyanopropene

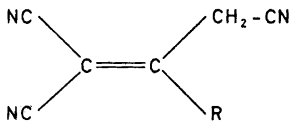
BERNT KLEWE

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystals are orthorhombic, space group *Pbca*, with lattice parameters $a = 16.94_7$ Å, $b = 16.19_5$ Å, and $c = 7.19_9$ Å. 1354 reflections were recorded as observed on an automatic four-circle diffractometer. The structure was refined by full-matrix least squares technique ($R_w = 3.7$ %, $R = 4.5$ %). The anion is propellershaped, the two $C(CN)_2$ arms (approximately related by a two-fold symmetry axis) being rotated 5.5° from the planar conformation. Short contacts between the $C(CN)_2$ groups are avoided by increasing bond angles to 125° and by decreasing the C–C–C angles within the $C(CN)_2$ groups to about 114°. The dihedral angles $(NC)-CH_2-C-(C(CN)_2)$ are 66° and −115°. The $sp-sp^2$ C–C and sp^2-sp^2 C–C bond lengths are 1.425 Å and 1.391 Å, respectively. The K^+ ion is coordinated to six nitrogen atoms, arranged in the form of a distorted octahedron.

The chemistry of the weak cyanocarbon acid malononitrile, a versatile compound of exceptional reactivity, has recently been reviewed by Freeman.[1]

In the present and forthcoming papers, results from X-ray crystallographic studies of condensation products of malononitrile will be presented. The three compounds so far studied are the potassium salts of 2-cyanomethyl-1,1,3,3-tetracyanopropene (potassium 2-cyanomethyl-1,1,3,3-tetracyanopropenide) and 1,1,3-tricyanopropanone,[2] and the 2-amino-1,1,3-tricyanopropene [3] molecule. In the following, these investigations will be referred to as $KC_9N_5H_2$, $KC_6N_3OH_2$, and $C_6N_4H_4$, respectively. The anions and the molecule are highly resonance stabilized species, and may conveniently be represented by the formula



$KC_9N_5H_2$: R = $C(CN)_2^-$

$KC_6N_3OH_2$: R = O^-

$C_6N_4H_4$: R = NH_2

Salts of 2-cyanomethyl-1,1,3,3-tetracyanopropene have been investigated by Kelly *et al.*[4] Atkinson and Johnson [5] have shown that a trimer of malononitrile in fact is the ammonium salt of 2-cyanomethyl-1,1,3,3-tetracyanopropene, and that the free "acid", described by Kelly *et al.*, is a complex of the hydrocarbon and its sodium salt. Several analogs of the hydrocarbon in which the cyanomethyl group is substituted have been described by Middleton *et al.*[6]

The acid strengths of these compounds arise from the stability of the anions, which usually have been assumed to be planar, because this conformation would give maximum *p*-orbital overlap and resonance stabilization. However, for the divalent anion of hexacyanoisobutylene (2-dicyanomethylene-1,1,3,3-tetracyanopropanediide),[7,8] deviation from planarity has been observed. The crystal structure determination of the (divalent) *cis*-hexacyano-2-butenediide anion [9] is also in progress.

In a review of the cyano group chemistry,[10] references to crystal structures of compounds containing the $C(CN)_2$ group are given (see also Refs. 11 – 13).

CRYSTAL DATA

$KC_9N_5H_2$ was synthesized from K_2CO_3 and melted malononitrile (55°C) by cand. mag. E.G. Iversen.

The light yellow needle-formed crystals (grown from aqueous solution) belong to the orthorhombic system, the systematic absences leading to the space group *Pbca*. A crystal of dimensions $0.27 \times 0.26 \times 0.13$ mm^3 was used for all X-ray measurements. The cell dimensions, determined at room temperature on a manual four circle diffractometer (Cu$K\beta$ radiation), and their estimated standard deviations are:

$a = 16.947(2)$ Å, $b = 16.195(2)$ Å, $c = 7.199(1)$ Å. c is the needle axis.

The cell contains eight formula units ($\varrho_{calc} = 1.472$ g cm^{-3}, $\varrho_{obs} = 1.47$ g cm^{-3}).

About 2200 reflections with $2\theta < 55°$ were measured (Mo$K\alpha$ radiation, 0.002″ Nb filter) on an automatic four circle diffractometer with the $\omega/2\theta$ scan technique. 1354 reflections with intensities greater than twice the standard deviation from counter statistics, including a 2 % uncertainty in scaling of intensities and fluctuation in diffractometer stability, were corrected for absorption and used in the structure determination.

All programs used are included in Ref. 14.

STRUCTURE DETERMINATION

The structure was solved by the heavy atom method and refined by full-matrix least squares technique to an R_w-value of 3.7 % (conventional R-value 4.5 %). Correction for secondary extinction effect did not lower the R-values, and was therefore neglected. Weight analysis showed that weighting based on the standard deviations was very satisfactory. Atomic form factors were those of Cromer and Waber,[15] except for hydrogen.[16] A final difference Fourier map contained no larger density fluctuations than ± 0.28 e Å^{-3}.

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	0	2	2331	-2623
0	0	4	697	707
0	0	6	495	- 484
0	0	8	144	141
0	2	0	307	- 309
0	2	1	101	- 85
0	2	2	105	96
0	2	3	1365	1378
0	2	4	264	266
0	2	5	436	- 444
0	2	6	355	- 365
0	2	7	277	269
0	2	8	71	83
0	2	9	134	- 139
0	4	0	396	- 384
0	4	1	337	- 337
0	4	2	1005	1001
0	4	3	948	946
0	4	4	646	- 643
0	4	5	485	- 489
0	4	6	329	336
0	4	7	238	224
0	4	8	218	- 233
0	4	9	177	- 157
0	6	0	1037	-1058
0	6	1	885	859
0	6	2	898	906
0	6	3	321	326
0	6	4	318	- 320
0	6	5	201	203
0	6	6	209	200
0	6	7	82	69
0	6	8	113	- 116
0	8	0	1510	-1518
0	8	1	846	856
0	8	2	366	339
0	8	3	620	- 621
0	8	4	270	- 274
0	8	5	555	522
0	8	6	166	174
0	8	7	192	- 188
0	8	8	82	- 11
0	10	0	296	299
0	10	1	381	382
0	10	2	200	- 207
0	10	3	70	- 81
0	10	4	168	170
0	10	5	153	146
0	10	6	161	- 170
0	10	7	193	- 171
0	10	8	160	155
0	12	0	335	339
0	12	1	430	- 434
0	12	2	735	- 746
0	12	3	309	321
0	12	4	434	459
0	12	6	84	- 108
0	14	0	172	- 169
0	14	2	128	- 133
0	14	3	114	- 117
0	14	4	207	203
0	14	5	115	- 97
0	14	6	110	- 106
0	16	1	413	- 418
0	16	3	176	178
0	16	5	135	- 89
0	18	0	101	- 89
0	18	1	143	- 135
0	18	4	142	- 139
0	20	0	124	- 118
0	20	1	287	276
0	20	2	251	250
1	0	2	607	- 606
1	0	4	142	- 138
1	0	6	269	279
1	0	8	193	- 205
1	1	1	278	273
1	1	2	1146	1144
1	1	3	163	168
1	1	4	103	- 105
1	2	1	227	219
1	2	2	456	- 448
1	2	3	223	- 216
1	2	4	217	- 221
1	2	8	74	90
1	3	1	537	- 527
1	3	2	448	- 443
1	3	3	51	- 50
1	3	4	191	188
1	4	1	819	788
1	4	2	39	24
1	4	4	37	- 22
1	4	5	288	- 291
1	4	7	94	92
1	5	1	140	134
1	5	2	94	- 97
1	5	3	229	225
1	5	4	62	67
1	5	5	72	72
1	6	1	88	- 82
1	6	2	51	- 37
1	6	3	124	128
1	6	4	161	159
1	6	6	95	- 96
1	7	1	310	- 309
1	7	2	48	- 32
1	7	3	118	- 121
1	7	4	118	121
1	7	5	57	63
1	7	6	87	86
1	8	1	396	387
1	8	2	42	51
1	8	3	234	- 235
1	8	5	93	114
1	8	8	87	80
1	9	1	97	90
1	9	2	325	- 323
1	9	3	177	- 184
1	9	4	95	- 90
1	9	5	57	- 72
1	9	7	90	65
1	10	1	41	35
1	10	2	278	275
1	10	3	142	147
1	10	5	108	- 103
1	10	6	111	98
1	11	1	63	46
1	11	2	114	113
1	12	1	53	52
1	12	2	59	- 46
1	12	3	180	- 182
1	12	4	77	70
1	12	5	110	118
1	12	7	80	- 95
1	13	2	88	99
1	13	3	163	- 154
1	13	4	178	- 190
1	13	5	85	76
1	14	2	346	336
1	14	3	125	133
1	14	4	98	- 94
1	14	5	145	- 145
1	15	2	78	- 75
1	15	3	93	94
1	16	1	171	- 177
1	16	3	128	140
1	20	2	117	- 105
2	0	0	451	- 488
2	0	2	876	869
2	0	4	145	148
2	0	6	301	- 310
2	0	8	191	176
2	1	0	264	- 254
2	1	2	79	- 64
2	1	3	210	208
2	1	4	416	- 402
2	1	5	160	- 156
2	1	6	220	223
2	1	7	96	109
2	2	0	1113	1098
2	2	1	1346	-1368
2	2	2	933	- 930
2	2	3	948	947
2	2	4	352	347
2	2	5	288	- 278
2	2	6	221	- 231
2	2	7	192	189
2	3	0	322	- 324
2	3	1	211	213
2	3	2	786	769
2	3	3	385	- 373
2	3	4	176	- 176
2	3	6	61	- 95
2	4	0	63	54
2	4	1	969	- 933
2	4	2	167	178
2	4	3	725	735
2	4	4	60	- 67
2	4	5	464	- 462
2	4	7	168	169
2	4	9	136	- 91
2	5	0	510	- 498
2	5	1	776	762
2	5	2	333	323
2	5	3	429	417
2	5	4	113	112
2	5	7	150	- 143
2	6	0	877	- 871
2	6	1	379	- 364
2	6	2	1004	1009
2	6	3	390	399
2	6	4	652	- 650
2	6	5	67	72
2	6	6	405	415
2	6	8	227	- 233
2	7	0	245	- 240
2	7	1	473	- 448
2	7	2	255	- 254
2	7	3	82	- 74
2	7	4	225	224
2	7	5	158	166
2	8	0	473	- 497
2	8	1	576	576
2	8	2	68	68
2	8	3	292	- 293
2	8	4	184	- 187
2	8	5	210	218
2	8	6	181	167
2	8	7	75	- 103
2	8	8	84	- 96
2	9	0	247	245
2	9	1	70	- 84
2	9	2	79	- 72
2	9	4	178	- 174
2	9	5	74	64
2	9	7	75	51
2	10	0	367	361
2	10	1	845	869
2	10	2	260	- 259
2	10	3	613	- 613
2	10	4	203	207
2	10	5	367	372
2	10	6	73	- 63
2	10	7	239	- 223
2	11	0	242	- 242
2	11	1	294	- 296
2	11	2	87	- 79
2	11	5	99	83
2	12	0	245	237
2	12	1	340	352
2	12	2	389	- 391
2	12	3	222	- 228
2	12	4	284	296
2	12	5	141	136
2	12	6	173	- 173
2	13	0	395	400
2	13	1	55	42
2	13	2	169	- 163
2	13	4	209	- 212
2	13	6	155	136
2	14	0	240	239
2	14	1	654	- 673
2	14	2	292	- 284
2	14	3	446	449
2	14	4	180	176
2	14	5	343	- 335
2	14	6	112	- 97
2	15	0	276	- 265
2	15	1	149	141
2	15	4	72	84
2	16	0	149	- 155
2	16	1	244	- 240
2	16	2	188	182
2	16	3	206	206
2	16	4	108	- 107
2	16	5	211	- 197
2	17	0	65	- 29
2	17	4	81	- 73
2	18	0	369	- 380
2	18	2	318	302
2	18	4	205	- 210
2	20	0	79	82
3	0	2	1217	-1240
3	0	4	361	353
3	0	6	142	- 151
3	0	8	106	113
3	1	1	98	- 106
3	1	2	1042	-1052
3	1	4	508	502
3	1	5	75	69
3	1	6	80	- 70
3	2	1	78	87
3	2	2	481	- 489
3	2	3	73	- 66
3	2	4	576	- 567
3	2	5	81	- 89
3	2	7	65	- 43
3	2	8	84	30
3	3	1	201	199
3	3	2	408	401
3	3	3	364	- 358
3	3	4	347	- 342
3	4	1	1466	1445
3	4	2	159	- 158
3	4	3	290	- 281
3	4	5	58	- 48
3	4	7	105	- 106
3	5	1	176	169
3	5	3	73	72
3	5	4	71	- 75
3	5	7	67	- 11
3	6	2	289	276
3	7	1	110	105
3	7	2	210	206
3	7	3	50	- 34
3	7	5	61	- 60
3	7	6	79	- 83
3	8	1	316	316
3	8	2	152	157
3	8	3	136	139
3	8	4	87	- 93
3	8	5	154	- 163
3	8	6	74	77
3	8	8	88	- 74
3	9	1	196	- 192
3	9	3	215	215
3	9	8	94	- 79
3	10	1	179	189
3	10	2	225	226
3	10	3	49	- 27
3	10	4	193	196
3	11	3	92	104
3	11	4	73	- 78
3	11	6	94	103
3	12	1	207	- 205
3	12	3	141	137
3	12	4	86	98
3	12	5	178	- 162
3	13	1	67	- 81
3	13	2	164	- 177
3	13	3	141	138
3	13	4	183	191
3	13	5	179	- 164
3	14	1	58	77
3	14	2	181	186
3	14	3	113	- 106
3	14	4	99	78
3	14	5	102	90
3	14	6	93	- 79
3	15	1	80	84
3	15	2	59	20
3	15	3	156	- 155
3	15	5	102	119
3	16	1	161	- 160
3	16	4	90	98
3	16	5	84	91
3	17	4	90	82
3	18	1	71	- 55
4	0	0	126	- 115
4	0	2	1755	-1843
4	0	4	1568	1592
4	0	6	523	- 526
4	0	8	232	237
4	1	0	183	181
4	1	1	158	- 163
4	1	2	655	- 633
4	1	3	224	221
4	1	4	73	62
4	1	5	94	- 87
4	1	6	56	- 30
4	2	0	534	537
4	2	1	1226	-1224
4	2	2	699	- 682
4	2	3	234	233
4	2	4	126	129
4	2	5	312	- 311
4	2	7	230	223
4	2	8	116	104
4	3	0	128	125
4	3	1	886	- 866
4	3	2	321	330
4	3	3	94	103
4	3	4	64	- 57
4	3	5	86	- 91
4	3	6	95	102
4	3	7	67	- 77
4	4	0	1365	-1354
4	4	1	1314	-1319
4	4	2	724	695
4	4	3	377	387
4	4	4	395	- 399
4	4	5	379	- 377
4	4	6	237	238
4	4	7	208	198
4	4	8	79	- 77
4	5	0	319	298
4	5	1	614	612
4	5	2	79	91
4	5	3	76	- 80
4	5	4	102	- 112
4	5	5	187	182
4	5	6	186	188
4	5	8	145	- 147
4	6	0	532	- 551
4	6	1	72	- 73
4	6	2	584	590
4	6	3	339	- 346
4	6	4	485	- 487
4	6	5	87	- 75
4	6	6	251	237
4	7	0	130	- 115
4	7	1	648	629
4	7	2	140	- 137
4	7	3	361	- 363

Table 1. Continued.

h	k	l	F_o	F_c
4	7	5	89	95
4	8	0	146	- 143
4	8	1	717	713
4	8	2	446	454
4	8	3	543	- 545
4	8	4	337	- 336
4	8	5	295	302
4	8	6	156	137
4	8	7	333	- 337
4	8	8	85	- 100
4	9	0	157	162
4	9	1	43	- 33
4	9	2	40	32
4	9	4	162	162
4	9	5	100	96
4	9	7	103	- 85
4	10	0	311	313
4	10	1	140	143
4	10	2	231	- 233
4	10	3	391	- 387
4	10	4	230	225
4	10	5	160	146
4	11	0	112	111
4	11	1	195	196
4	11	2	291	- 296
4	11	3	113	116
4	11	4	88	84
4	11	5	126	- 122
4	11	7	138	167
4	12	0	740	748
4	12	1	109	- 112
4	12	2	369	- 365
4	12	4	297	290
4	12	5	77	- 65
4	12	6	329	- 320
4	13	0	366	- 372
4	13	1	503	- 527
4	13	2	173	176
4	13	3	234	241
4	13	5	155	- 150
4	14	0	407	414
4	14	2	176	- 177
4	14	3	107	115
4	15	0	148	- 132
4	15	2	158	141
4	15	4	119	- 129
4	15	6	125	119
4	16	0	169	- 163
4	16	1	120	- 132
4	16	2	186	186
4	16	3	222	214
4	16	4	81	- 85
4	16	5	164	- 170
4	17	1	150	135
4	17	3	145	- 147
4	18	0	167	- 178
4	18	2	126	138
4	18	3	165	169
4	18	4	100	- 91
4	19	0	110	115
4	20	0	326	- 318
4	20	1	122	105
5	0	2	851	839
5	0	4	425	- 407
5	0	6	175	185
5	1	2	161	- 165
5	1	3	220	- 214
5	1	4	401	- 401
5	1	5	69	89
5	1	6	284	280
5	1	7	68	- 24
5	2	1	420	- 408
5	2	2	66	- 59
5	2	3	190	185
5	2	4	44	- 26
5	2	5	119	- 119
5	2	6	62	- 69
5	3	1	62	74
5	3	2	119	120
5	3	3	216	212
5	3	5	100	- 105
5	3	6	73	- 41
5	3	7	71	- 60
5	4	2	123	- 122
5	4	3	352	374
5	5	1	105	108
5	5	2	36	28
5	5	3	252	- 258
5	5	7	80	59
5	6	2	134	- 128
5	6	3	60	- 58
5	6	4	128	124
5	6	5	215	- 219
5	6	6	93	82
5	6	7	69	15
5	7	1	119	117
5	7	3	214	213
5	7	4	64	- 61
5	7	5	175	- 187
5	8	3	97	96
5	8	4	85	94
5	8	5	73	- 72
5	8	6	160	- 160
5	9	1	75	- 72
5	9	2	144	154
5	9	3	141	152
5	9	4	177	183
5	9	6	135	- 142
5	10	1	120	117
5	10	2	74	- 68
5	10	3	108	- 111
5	10	4	185	186
5	10	5	99	101
5	11	1	50	38
5	11	2	129	- 133
5	12	1	117	- 116
5	12	2	182	186
5	12	3	92	- 82
5	12	4	73	- 84
5	12	5	100	104
5	13	1	113	106
5	13	2	68	82
5	13	3	126	- 126
5	13	5	188	172
5	14	2	222	- 225
5	14	4	65	52
5	15	2	63	86
5	16	1	65	56
5	16	2	95	106
5	16	3	107	- 98
5	19	1	119	- 115
5	19	2	136	118
6	0	0	107	125
6	0	2	1101	-1125
6	0	4	256	262
6	0	6	78	80
6	1	0	1623	-1639
6	1	1	636	- 639
6	1	2	825	788
6	1	3	503	504
6	1	4	368	- 372
6	1	5	182	- 186
6	1	7	108	106
6	2	0	145	156
6	2	1	672	- 673
6	2	2	398	- 413
6	2	3	443	440
6	2	4	373	376
6	2	5	619	- 628
6	2	6	105	- 113
6	2	7	279	298
6	2	8	118	159
6	3	0	607	- 612
6	3	1	495	498
6	3	2	402	394
6	3	3	233	- 240
6	3	4	277	- 286
6	3	6	376	380
6	3	7	98	- 74
6	3	8	199	- 201
6	4	0	335	- 335
6	4	1	948	- 940
6	4	2	61	- 37
6	4	3	264	279
6	4	4	74	- 72
6	4	5	233	- 227
6	4	6	159	150
6	4	7	124	113
6	4	8	76	- 45
6	5	0	249	- 240
6	5	1	72	- 58
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6	7	2	432	- 429
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6	8	3	415	- 419
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6	9	5	221	- 202
6	9	6	185	- 172
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6	10	1	438	443
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6	10	3	465	- 474
6	10	4	179	179
6	10	5	335	333
6	10	6	276	- 272
6	10	7	192	- 195
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6	11	1	305	- 304
6	11	3	279	287
6	11	5	97	- 112
6	12	0	542	544
6	12	1	101	111
6	12	2	181	- 182
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6	13	1	223	230
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6	14	5	152	- 140
6	14	6	175	- 161
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6	15	1	103	- 113
6	15	2	138	135
6	15	4	126	- 114
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7	11	3	159	- 169
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7	12	2	93	- 91
7	12	3	154	- 143
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7	12	6	116	- 95
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7	13	3	202	204
7	13	4	125	- 120
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7	13	6	83	13
7	14	2	115	- 114
7	14	3	108	99
7	14	4	100	- 119
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7	16	5	95	- 86
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8	0	6	373	- 364
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8	1	5	156	- 152
8	1	7	143	151
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8	3	3	166	163
8	3	4	221	- 223
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8	4	3	553	559
8	4	4	226	- 228
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8	5	2	249	248
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8	8	4	154	- 148
8	8	5	339	346
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8	8	7	91	- 75
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8	9	2	228	- 231
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8	12	6	151	- 163
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8	14	3	175	179
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8	15	2	240	225
8	15	4	181	- 175
8	16	0	146	- 147
8	16	1	120	- 114
8	16	3	169	162
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8	17	1	230	226
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8	18	2	156	147
8	19	0	144	146

Table 1. Continued.

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9	2	6	76	107
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9	3	6	105	98
9	4	1	82	- 92
9	4	3	247	- 243
9	4	4	243	265
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9	4	6	120	- 129
9	4	8	82	- 42
9	5	1	293	- 297
9	5	2	129	135
9	5	3	135	134
9	5	4	65	- 66
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9	6	1	181	- 177
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9	6	4	243	- 250
9	6	5	222	214
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9	7	3	156	160
9	7	4	53	- 50
9	8	1	218	- 226
9	8	2	239	- 247
9	8	3	149	158
9	9	2	180	- 181
9	9	3	58	- 69
9	9	4	69	86
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9	11	1	167	- 167
9	11	2	72	57
9	11	3	113	97
9	11	5	87	- 81
9	11	6	97	- 71
9	12	2	143	- 126
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9	12	4	100	- 98
9	12	5	150	- 155
9	13	1	101	85
9	13	2	106	- 111
9	13	3	93	- 83
9	13	5	137	113
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11	4	3	71	- 65
11	4	4	57	- 79
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11	6	6	77	- 62
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11	12	3	79	- 74
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12	0	6	97	- 110
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12	1	2	248	249
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12	4	4	75	- 93
12	4	5	189	- 182
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12	5	1	438	431
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12	5	3	331	- 333
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12	7	2	242	- 245
12	7	3	245	- 245
12	7	5	242	237
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12	8	3	108	- 101
12	8	5	82	82
12	9	1	282	289
12	9	2	244	- 240
12	9	4	228	225
12	9	6	216	- 209
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12	10	3	137	- 118
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12	11	0	75	50
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12	12	0	173	187
12	12	1	118	128
12	12	2	216	- 218
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13	13	0	184	- 181
13	13	1	280	- 276
13	13	2	73	67
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14	0	2	224	- 233
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14	1	2	269	205
14	1	3	231	232
14	1	4	121	- 125
14	1	5	238	- 241
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14	2	0	82	85
14	2	1	226	- 230
14	2	2	241	- 249
14	2	3	262	263
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14	4	0	96	- 85
14	4	1	133	153
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14	5	2	181	186
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14	7	2	104	- 87
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14	9	1	113	- 101
14	9	2	298	- 287
14	9	3	110	89
14	9	4	232	221
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14	14	0	121	106
14	15	0	121	- 111
14	15	2	100	121
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15	0	4	117	- 121
15	0	6	78	97
15	1	1	81	76
15	1	2	154	153
15	1	4	80	- 23
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15	5	2	122	106
15	5	4	125	- 125
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15	6	2	108	105
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15	7	4	96	102
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15	11	1	73	40
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15	12	2	127	138
15	14	1	102	- 91
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16	1	0	292	- 286
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16	1	2	258	260
16	1	3	224	220
16	1	4	198	- 195
16	1	5	199	- 194
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16	2	1	102	113
16	3	0	320	- 317
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16	3	2	299	292
16	3	4	225	- 217
16	3	6	107	124
16	4	1	409	- 408
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16	5	2	94	106
16	5	3	218	- 213
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Table 1. Continued.

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16	7	4	168	165
16	7	5	152	143
16	8	3	218	- 210
16	9	0	377	376
16	9	1	70	- 21
16	9	2	305	- 300
16	9	4	180	182
16	10	0	117	113
16	10	1	87	80
16	10	2	144	148
16	10	4	122	- 112
16	11	0	127	113
16	11	1	288	- 281
16	11	3	117	146
16	12	0	146	136
16	12	1	131	126
16	13	1	78	- 33
16	13	2	94	79
17	1	1	66	45
17	1	2	102	56
17	1	4	80	67
17	1	5	81	47
17	2	3	85	- 86
17	3	1	114	- 106
17	3	4	100	- 97
17	4	2	124	112
17	4	4	92	12
17	5	1	114	104
17	5	2	88	- 74
17	6	1	137	- 134
17	6	2	110	101
17	7	1	85	- 56
17	7	2	155	146
17	8	1	70	- 64
17	9	3	97	89
17	10	1	83	- 71
17	10	3	97	83
17	12	2	129	- 114
18	0	2	109	88
18	1	0	98	- 87
18	1	1	291	- 285
18	1	3	187	188
18	1	4	88	- 65
18	2	1	78	- 85
18	2	2	134	- 133
18	3	0	122	- 132
18	3	1	67	- 47
18	3	2	224	225
18	3	4	229	- 237
18	3	5	89	- 69
18	4	2	85	72
18	4	3	139	- 148
18	5	0	135	- 151
18	5	1	251	257
18	5	2	119	104
18	5	3	133	- 135
18	6	0	121	121
18	6	2	75	45
18	6	3	91	36
18	6	4	149	- 129
18	7	0	102	90
18	7	1	225	220
18	7	2	173	- 173
18	7	3	249	- 231
18	7	4	91	82
18	8	0	167	- 171
18	8	3	115	61
18	9	0	214	204
18	9	2	98	- 116
18	11	1	146	- 158
19	0	2	122	119
19	1	2	86	- 68
19	1	3	79	69
19	2	1	109	- 82
19	4	3	117	113
19	5	3	79	71
19	6	1	94	- 99
19	6	2	90	- 71
20	1	0	254	- 264
20	1	1	147	- 133
20	1	2	121	113
20	1	3	200	198
20	2	2	97	113
20	2	3	90	- 53
20	3	0	249	- 234
20	3	2	263	220
20	3	3	102	- 88
20	4	0	116	120
20	4	1	109	65
20	4	3	94	60
20	5	0	136	- 135
20	5	1	95	112
20	5	2	108	111
20	7	0	91	108
20	7	1	108	125
21	0	2	100	82
21	4	1	95	54

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

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K^+	1398	8267	25007	252	289	1785	69	65	152
	3	3	9	2	2	13	4	11	12
C1	32202	32714	18251	209	183	1355	20	−72	102
	14	13	34	10	9	56	15	40	38
C2	24724	33695	25614	222	174	1047	24	−198	−40
	13	12	32	10	9	42	13	45	42
C3	21829	42460	28930	225	159	1685	32	−33	−115
	13	13	33	10	8	69	15	37	39
C4	36133	24959	16554	222	292	1811	30	107	82
	13	17	37	10	11	66	20	45	53
C5	36737	39626	12089	212	266	1533	82	−37	−149
	14	16	37	10	11	64	18	43	47
C6	15021	44610	17315	365	203	1586	127	229	−171
	17	15	39	13	11	67	20	51	46
C7	19587	27354	30839	212	182	1406	−5	−21	−56
	13	13	32	9	10	62	15	38	38
C8	20891	18796	28031	268	241	1152	−93	30	19
	14	14	33	10	11	64	17	40	43
C9	12184	29249	39266	268	236	1544	−132	−4	−29
	16	15	37	12	11	66	18	47	46
N4	39449	18867	15344	371	348	3863	266	229	106
	14	14	39	11	11	82	18	52	53
N5	40397	45164	6926	308	307	2524	−100	371	34
	13	12	32	10	10	66	17	43	41
N6	9729	46305	8459	449	464	2395	379	−547	−338
	15	14	34	11	12	68	20	50	46
N8	21446	11821	25841	478	210	2359	−47	12	−11
	13	12	34	12	8	59	16	46	43
N9	6297	30780	46233	295	500	2584	−49	385	−221
	13	14	35	11	12	68	18	43	48
H1	25873	46406	27194	3.74					
	134	142	335	.57					
H2	20113	43188	43394	3.95					
	133	127	351	.59					

Table 3. The root mean square amplitudes of vibration $(\overline{u^2})^{1/2}$ (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	$(\overline{u^2})^{1/2}$	B	e_x	e_y	e_z
	.224	3.95	17	28	117
K+	.199	3.12	37	36	−73
	.180	2.57	43	−42	15
	.192	2.91	−16	12	131
Cl	.174	2.39	55	20	29
	.152	1.82	15	−57	38
	.192	2.90	48	9	−77
C2	.153	1.84	34	−7	113
	.151	1.80	−3	61	25
	.212	3.54	7	9	−137
C3	.182	2.60	58	9	19
	.142	1.60	−10	60	18
	.221	3.87	13	16	131
C4	.196	3.02	9	58	−42
	.177	2.46	−57	13	23
	.210	3.49	19	36	−104
C5	.189	2.81	31	34	90
	.164	2.12	−47	37	18
	.240	4.55	54	13	47
C6	.205	3.33	14	26	−122
	.148	1.72	−19	55	47
	.193	2.94	6	8	−137
C7	.175	2.43	59	−5	12
	.154	1.88	4	61	18
	.207	3.39	51	−31	6
C8	.175	2.42	9	21	129
	.167	2.19	29	49	−50
	.212	3.57	49	−34	12
C9	.201	3.20	−6	0	138
	.159	1.99	33	51	7
	.321	8.14	11	7	136
N4	.260	5.32	44	39	−30
	.176	2.46	−37	48	4
	.267	5.64	24	−4	126
N5	.217	3.71	−36	45	45
	.183	2.64	40	42	−36
	.316	7.88	40	36	−64
N6	.232	4.25	11	29	120
	.190	2.85	43	−41	29
	.264	5.51	59	−5	7
N8	.249	4.89	3	0	−139
	.166	2.19	5	62	1
	.278	6.12	19	−34	107
N9	.248	4.87	11	51	73
	.195	3.01	55	2	−51

A comparison between observed and calculated structure factors is presented in Table 1, and the final parameters with estimated standard deviations are given in Table 2. For numbering of atoms, see Fig. 1.*

* A similar numbering is used for KC_6N_3OH and $C_6N_4H_4$.

The principal axes of the thermal vibration ellipsoids, calculated from the thermal parameters of Table 1, the root mean square amplitudes, and the corresponding B-values are given in Table 3.

The anion can hardly be regarded as an oscillating rigid body. The r.m.s. discrepancy between "observed" atomic vibration tensor components and those calculated from the rigid-body parameters obtained by analysis of librational, translational, and screw motion [17] is as large as 0.0054 Å^2. By excluding the cyano group C6–N6 of the $-CH_2(CN)$ group, the r.m.s. discrepancy drops to 0.0040 Å^2. A further reduction (to 0.0030 Å^2) is obtained by omitting C6 and all nitrogens. However, when three cyano groups, C6–N6 and two others, are not included in the analysis, negative eigenvalues in **L** come out. The reduced r.m.s. translational amplitudes corresponding to the

Table 4. Bond distances, bond angles, and dihedral angles of the anion, short *intra*-molecular contacts, and non-bonded distances between anions (equivalent position numbers in parentheses, as defined in Table 6). Estimated standard deviations in C–C and C–N bond lengths are 0.003 Å, and in C–C–C and C–C–N angles 0.2° and 0.3°, respectively. Distances in parentheses are corrected for anisotropic thermal motion (see text).

Bond distances (Å)

C1–C2	1.383	(1.388)
C2–C3	1.521	(1.525)
C1–C4	1.427	(1.432)
C1–C5	1.429	(1.432)
C3–C6	1.467	(1.471)
C2–C7	1.398	(1.402)
C7–C8	1.418	(1.423)
C7–C9	1.427	(1.431)
C4–N4	1.139	(1.183)
C5–N5	1.152	(1.183)
C6–N6	1.134	(1.180)
C8–N8	1.145	(1.172)
C9–N9	1.144	(1.180)
C3–H1	.95	
C3–H2	1.09	

Intra-molecular contacts (Å)

C3···C5	2.83
C3···C9	2.79
C4···C8	2.89
C6···C9	2.99
C5···H1	2.40

Other contacts (Å)

C8···N9(2)	3.37
C8···C9(2)	3.17
N8···C9(2)	3.39
N8···H2(2)	2.48
N8···C6(3)	3.34
N8···N6(3)	3.35
N8···C3(4)	3.34
N8···H1(4)	2.54

Bond angles (°)

C4–C1–C2	124.2
C5–C1–C2	121.5
C4–C1–C5	114.3
C1–C2–C3	117.6
C1–C2–C7	126.1
C7–C2–C3	116.3
C2–C3–C6	112.7
C8–C7–C2	125.6
C9–C7–C2	120.3
C8–C7–C9	114.1
C1–C4–N4	178.2
C1–C5–N5	179.3
C3–C6–N6	179.4
C7–C8–N8	175.7
C7–C9–N9	179.1
C2–C3–H1	112
C2–C3–H2	110
C6–C3–H1	110
C6–C3–H2	108
H1–C3–H2	104

Dihedral angles (°)

C4–C1–C2–C3	−171.7
C5–C1–C2–C3	6.6
C4–C1–C2–C7	6.5
C5–C1–C2–C7	−175.3
C1–C2–C3–C6	−115.4
C7–C2–C3–C6	66.3
C8–C7–C2–C3	−176.2
C9–C7–C2–C3	1.7
C8–C7–C2–C1	5.7
C9–C7–C2–C1	−176.4

discrepancy of 0.0040 Å^2 are 0.184, 0.157, and 0.141 Å, while the r.m.s. librational amplitudes are 4.8, 3.3, and 2.7°. The eigenvectors of the atomic vibration tensor of C2 correspond closely to those of **T**.

"Riding motion" corrections [18] show that C1, C3, and C7 are "riding" on C2. Contrary to what might be expected, C5 and C8 do not "ride" on C1 and C7, respectively. No program for "segmented rigid-body" calculation has been available.

Bond distances, bond angles, and dihedral angles of the anion, short *intra*-molecular contacts, and non-bonded distances between anions may be found in Table 4. The C–N bond distances in parentheses are corrected for "riding motion". Librational corrections in other bonds, all less than twice the standard deviation in bond lengths, correspond to the rigid body calculation of the anion with C6–N6 omitted. The estimated standard deviations in C–C and C–N bond lengths of 0.003 Å, and in C–C–C and C–C–N angles of 0.2° and 0.3°, respectively, have been calculated from the correlation matrix of the last least squares refinement cycle without taking into account the E.S.D.'s of the cell parameters. Bond distances (uncorrected) and angles are also given in Fig. 1.

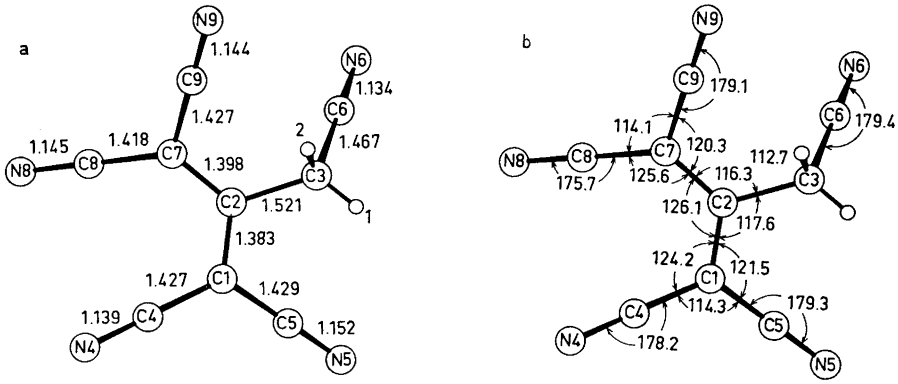

Fig. 1. Schematical drawings of the anion, showing bond distances (a) and bond angles (b). Small circles indicate hydrogen atoms.

The deviations of atoms from some least squares planes through the anion are listed in Table 5, while coordination distances of the cation is presented in Table 6. Fig. 2 is a schematical drawing of the structure, showing the packing and coordination viewed along the *c* axis.

DISCUSSION

The geometry of the anion will first be discussed.

The two $C(CN)_2$ groups bonded to C2 are approximately related by a two-fold axis of symmetry. This can be seen by examination of the bond distances and angles of Fig. 1, together with the deviations from the least squares plane

Table 5. Deviations of atoms from some least squares planes (Å). Plane No. 1 is through all atoms except the $CH_2(CN)$ group, planes Nos. 2 and 3 through the $C-C(CN)_2$ groups, and planes Nos. 4 and 5 through the $C(CN)_2$ groups, respectively. Deviations of atoms not defining the planes in parentheses.

Atom	1	2	3	4	5
C1	0.016	−0.012		0.001	
C2	0.009	0.008	−0.011	(0.039)	(−0.050)
C3	(0.065)				
C4	0.140	−0.013		−0.009	
C5	−0.067	0.003		0.006	
C7	−0.008		0.014		−0.002
C8	−0.136		0.016		0.012
C9	0.062		−0.004		−0.008
N4	0.261	0.010		0.005	
N5	−0.146	0.002		−0.003	
N8	−0.267		−0.012		−0.006
N9	0.137		−0.002		0.004

Table 6. Coordination distances of the potassium ion and $C-N\cdots K^+$ angles. For numbering of equivalent positions, see Fig. 2.

Atom	Equiv. pos.	No.	(Å)	(°)
N4	$(-\frac{1}{2}+x, y, \frac{1}{2}-z)$	1	2.74	153
N9	$(x, \frac{1}{2}-y, -\frac{1}{2}+z)$	2	2.85	135
N6	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3	2.89	143
N5	$(\frac{1}{2}-x, -\frac{1}{2}+y, z)$	4	2.85	134
N6	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	5	2.95	116
N5	$(-\frac{1}{2}+x, \frac{1}{2}-y, -z)$	6	3.01	116

through the atoms involved (plane 1 of Table 5). The deviations of "symmetry" related atoms differ less than 0.01 Å. The C2 – C3 bond, making an angle of 2° with this plane, is not colinear with the symmetry axis. The dihedral angle C7 – C2 – C3 – C6 is 66°. C6 and C3 are situated on opposite sides of plane 1.

The least squares planes through one of the $C(CN)_2$ groups and C2 (planes 2 and 3) make angles of 5.4° and 5.5° with plane 1. As shown by the calculation of least squares planes through the $C(CN)_2$ groups (planes 4 and 5), C2 is out of the planes by 0.039 Å and 0.050 Å, respectively. The bonds to C2 make angles of about 2° with these planes. A similar bending of the "planar" $C(CN)_2$ group is also observed for KC_6N_3OH and $C_6N_4H_4$. The small deviations from planarity may be due to short *intra*-ionic contacts as well as coordination and packing effects.

In the divalent anion of hexacyanoisobutylene [7,8] the $C(CN)_2$ arms are rotated up to 24° from the completely planar conformation. However, in the present ion, short contacts are avoided, mainly by opening of the angles C2 – C1 – C4, C1 – C2 – C3, and C2 – C7 – C8 to about 125° (the twist being only 5.5°). C – C – C angles of about 114° in the $C(CN)_2$ groups are in agree-

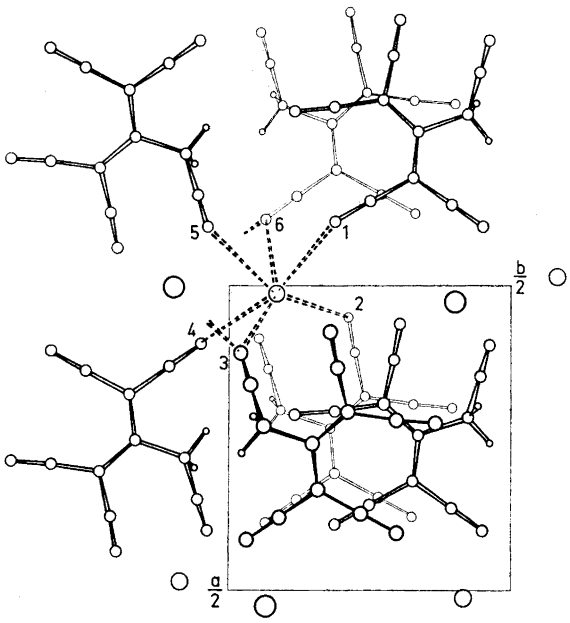

Fig. 2. Schematical drawing of the structure viewed along the *c* axis, showing the coordination. The equivalent positions of anions numbered from 1 to 6 are given in Table 6.

ment with earlier results.[7,8] A decrease of the angles C2 – C1 – C5 and C2 – C7 – C9 is hindered by the presence of the $CH_2(CN)$ group. This hindrance is reduced in the case of 1,1,3,3-tetracyanopropenide and 1,1,2,3,3-pentacyanopropenide anions, and crystal structure determinations of these are therefore planned.

Other bond angles are normal. The deviation of 4° from 180° of the C7 – C8 – N8 angle is probably due to packing effects. In all short contacts between anions, either C8 or N8 is involved (Table 4).

The thermal corrections of the C – N bonds, assuming "riding motion", are large (0.046 Å for C6 – N6). In spite of the consistency in corrected C – N bond values, the corrections may be based upon unwarranted assumptions. Corrections of other bond lengths, based upon "rigid – body" calculations, may also be questioned. Uncorrected values of the bond distances will therefore be discussed.

Molecular orbital calculations of π-electron densities of the 1,1,3,3-tetracyanopropenide anion (A) and the divalent anion of hexacyanoisobutylene (B) have been carried out by Lofthus, using a method[20] based on extended HMO theory. The π-bond order of the C – C bonds in the $C(CN)_2$ groups are 0.46 and 0.49, respectively. For the $sp^2 - sp^2$ carbon – carbon bonds, the values are 0.62 and 0.52, and for the C – N bonds, 0.81 and 0.79. The results for (B) are in good agreement with earlier calculations.[7] The calcu-

lated bond order values for (A) is in the following discussion assumed to be applicable also for the present anion. The mean value (1.425 Å) of the C – C bonds in the $C(CN)_2$ groups compared with the average (1.391 Å) for the bonds from the $C(CN)_2$ groups show that this assumption is reasonable. The corresponding values for (B) [7,8] are 1.427 Å and 1.420 Å, respectively (uncorrected). The difference in bond order between (A) and (B) for the latter bond of 0.1 predicts a difference of 0.027 Å,[19] which is in close agreement with the observed difference (0.029 Å). As may be expected, the agreement with similar simple calculations on TCNQ (7,7,8,8-tetracyanoquinodimethane) and $TCNQ^{-}$[19] is not so good.

The observed difference of 0.015 Å between the C1 – C2 and C2 – C7 (estimated standard deviations in bond lengths 0.003 Å) may not be significant, as they have one atom in common. The C2 – C3 distance of 1.521 Å is somewhat longer than expected for a $sp^2 - sp^3$ carbon – carbon bond. A similar value is found for $KC_6N_3OH_2$.

The packing is shown in Fig. 2. Nitrogen atoms from six different anions are coordinated to one cation, forming a distorted octahedron. The coordination distances and the corresponding $C-N\cdots K^+$ angles are given in Table 6. A correlation between coordination distance and carbon – nitrogen-cation angle is observed.[12] All nitrogen atoms but N8 are coordinated to K^+. The anion with atomic parameters of Table 2 is symmetry-related to the anions in positions 2 and 3 (Fig. 2) by a glide plane along c at $y = 1/4$. This anion is not coordinated to the cation of Table 2. The normal of plane 1 of Table 5 makes an angle of 89° with the b axis and 23° with the c axis, respectively. The assumption of the atoms being situated in a plane parallel to b, and making the same angle as 1 with c, corresponds to an anion "thickness" of 3.31 Å.

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