

The Crystal Structure of Dirubidium 1,1,2,2-Tetranitroethanediide, Space Group *Pccn*

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The crystals are orthorhombic, space group *Pccn*, with cell dimensions $a = 7.70_0$ Å, $b = 13.35_8$ Å, and $c = 8.84_1$ Å. 926 X-ray reflections were recorded as observed on an automatic four-circle diffractometer. The structure was refined by full-matrix least squares methods ($R_w = 7.9\%$, $R = 7.7\%$). The anions are centered on two-fold rotation axes. The angle between the essentially planar $C(NO_2)_2$ groups is 68° . The carbon atom and its three substituents are coplanar.

Infrared spectra of 1,1-dinitro-carbanion salts¹ and pK 's of 1,1-dinitro compounds² have been discussed in relation to their structures and a series of crystal structure determinations have been carried out.³⁻¹⁸

The stability of a carbanion depends largely on the efficiency with which the charge can be delocalized from its formal location on the acid carbon. Maximum resonance interaction would require total planarity for the $RC(NO_2)_2^-$ anion. Oxygen oxygen repulsions may cause some skewing of the nitro groups. An expansion of the N-C-N angle and corresponding decreased O...O repulsion should favour nitro coplanarity. A number of physical and chemical properties of these compounds are therefore quite sensitive to the steric requirements of R.^{1,2,13,19}

In a preliminary note on the crystal structure determination of dipotassium and dirubidium 1,1,2,2-tetranitroethanediide¹⁴ (based on two-dimensional data) three-dimensional studies of these were announced. The crystal structure of the potassium compound was independently determined by Dyke and Sass¹⁵ using three-dimensional data and work on that structure was accordingly discontinued. In the present paper the three-dimensional analysis of the rubidium salt is reported. During the further studies on this salt another crystal form was observed, and an investigation of this is being undertaken.

EXPERIMENTAL

The rubidium salt was directly prepared from rubidium iodide and tribromonitromethane following the procedure described by Hunter²⁰ for the synthesis of the potassium salt. The possibility of potassium contamination (present when prepared in a metathetic

reaction¹⁴) was thus avoided. Single crystals were grown by evaporation of aqueous solutions at room temperature or in refrigerator. Sometimes two crystal modifications were apparently simultaneously formed, both being well developed prismatic needles. The periods along the needle axes were 8.84 and 8.92 Å, respectively, and they were most easily identified by their Weissenberg diagrams.

The unit cell dimensions of the crystal form earlier investigated, space group *Pccn*, were determined on a manual four-circle diffractometer using CuK radiation. All diffractometer setting angles were optimized for 16 reflections used in the least squares refinement. The computer programs used are described in Ref. 21.

About 1000 reflections with $2\theta < 55^\circ$ and later 900 additional reflections with $55^\circ < 2\theta < 70^\circ$ were registered on an automatic four-circle diffractometer using MoK α radiation (highly oriented graphite monochromator) and $\omega/2\theta$ scan technique. A crystal of dimensions $0.19 \times 0.35 \times 0.40$ mm³ mounted with c^* along the ϕ axis of the diffractometer was used for the data collection. Possible errors caused by the Renninger effect have been ignored. The crystal was repeatedly dipped in liquid nitrogen but the increase in intensities of the standard reflections showed that the crystal still suffered from extinction effects. Accordingly the data with large 2θ values (high values for h) were first registered. When the intensities of the standard reflections approached constant values the reflections for which extinction corrections were assumed to be important were remeasured. An anisotropic destruction of the crystal occurred during the collection of high angle data, the decrease in intensities of the standard reflections varying from 0 to 45 %.

Different data sets were obtained by varying the criteria for intensities to be recorded as observed, as well as using the standard reflections for scaling or not. Only small differences were obtained in the estimated standard deviations of atomic parameters derived from different data sets. For the data set eventually used reflections having intensities greater than 2.5 times the standard deviations from counting statistics were considered to be observed. The reflections collected prior to stable standard reflections were not scaled, whereas the remaining standard reflections were used for intensity adjustment. A 4 % uncertainty in scaling and fluctuation of apparatus were included in the estimated standard deviations. The 926 reflections recorded as observed, of which 230 had $2\theta > 55^\circ$, were corrected for absorption. The linear absorption coefficient is 11.43 mm^{-1} and the transmission factor varied from 0.11 along a to 0.27 along b .

CRYSTAL DATA

Dirubidium 1,1,2,2-tetranitroethanediide $\text{Rb}_2\text{C}_2\text{N}_4\text{O}_8$, F.W. 379.0. Yellow prismatic needles (c), $\{110\}$ well developed, orthorhombic. $a = 7.700(1)$, $b = 13.358(2)$, $c = 8.841(1)$ Å, $V = 909.3(2)$ Å³. $F(000) = 704$; $Z = 4$; $\rho_{\text{calc}} = 2.768$ g cm⁻³; $\mu = 11.43 \text{ mm}^{-1}$. Space group *Pccn*, anions on two-fold axes.

STRUCTURE REFINEMENT

The atomic parameters from the two-dimensional analysis were used as starting parameters in the full-matrix least squares refinement. The strongest reflections (about 100) were excluded from the first refinement cycles. An R_w of 16.6 % was obtained with isotropic temperature factors. Inclusion of anisotropy for the rubidium atom lowered the value to 10.2 %. Refinement of anisotropic thermal parameters for all atoms resulted in an R_w of 8.3 %. The R_w factor ratio²² is 1.23, which justifies the inclusion of the latter parameters in the refinement. The conventional R value for all reflections decreased from 8.0 % to 7.7 % when corrections for secondary extinction were carried out; the final R_w was 7.9 %. The weight analysis based on the standard deviations in intensities showed a slight intensity dependence indicating that an

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

| h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | | | | | |
|-----|-----|-----|---------|---------|-----|-----|-----|---------|---------|-----|-----|-----|---------|---------|-----|-----|-----|---------|---------|---|----|----|------|-------|
| 0 | 0 | 2 | 210 | 216 | 1 | 1 | 4 | 187 | -203 | 1 | 13 | 5 | 84 | 32 | 2 | 11 | 8 | 170 | 186 | 3 | 12 | 6 | 149 | -123 |
| 0 | 0 | 4 | 1275 | -1368 | 1 | 1 | 5 | 143 | -173 | 1 | 13 | 6 | 114 | 93 | 2 | 11 | 10 | 211 | 197 | 3 | 12 | 10 | 161 | 167 |
| 0 | 0 | 6 | 989 | -1048 | 1 | 1 | 6 | 465 | -465 | 1 | 13 | 8 | 125 | 12 | 2 | 12 | 0 | 392 | -384 | 3 | 13 | 0 | 159 | 179 |
| 0 | 0 | 8 | 709 | -924 | 1 | 1 | 7 | 105 | -107 | 1 | 14 | 2 | 462 | 491 | 2 | 12 | 1 | 94 | -84 | 3 | 13 | 8 | 146 | -76 |
| 0 | 0 | 12 | 349 | 347 | 1 | 1 | 8 | 310 | -362 | 1 | 14 | 4 | 396 | 389 | 2 | 12 | 2 | 457 | -454 | 3 | 14 | 1 | 175 | 178 |
| 0 | 1 | 2 | 517 | -529 | 1 | 2 | 1 | 352 | 318 | 1 | 14 | 6 | 94 | 51 | 2 | 12 | 4 | 145 | 151 | 3 | 14 | 2 | 320 | -323 |
| 0 | 1 | 4 | 943 | -1055 | 1 | 2 | 2 | 895 | 916 | 1 | 14 | 8 | 136 | -131 | 2 | 12 | 6 | 393 | 391 | 3 | 14 | 4 | 377 | -382 |
| 0 | 1 | 6 | 142 | -130 | 1 | 2 | 3 | 757 | -771 | 1 | 14 | 10 | 180 | -160 | 2 | 12 | 8 | 261 | 200 | 3 | 14 | 10 | 167 | 121 |
| 0 | 1 | 8 | 188 | 194 | 1 | 2 | 4 | 974 | 1051 | 1 | 15 | 0 | 417 | 426 | 2 | 13 | 1 | 75 | 83 | 3 | 15 | 0 | 216 | -201 |
| 0 | 1 | 10 | 125 | 135 | 1 | 2 | 5 | 207 | -227 | 1 | 15 | 2 | 212 | 202 | 2 | 13 | 2 | 100 | -78 | 3 | 15 | 2 | 173 | -161 |
| 0 | 2 | 0 | 502 | 524 | 1 | 2 | 6 | 225 | 252 | 1 | 15 | 4 | 194 | -218 | 2 | 13 | 3 | 178 | 179 | 3 | 15 | 6 | 144 | 128 |
| 0 | 2 | 2 | 1246 | 1272 | 1 | 2 | 7 | 319 | 356 | 1 | 15 | 6 | 124 | -108 | 2 | 13 | 5 | 117 | 93 | 3 | 15 | 8 | 138 | 118 |
| 0 | 2 | 4 | 420 | -417 | 1 | 2 | 10 | 324 | -360 | 1 | 15 | 8 | 186 | -156 | 2 | 13 | 7 | 107 | -103 | 3 | 15 | 10 | 117 | 61 |
| 0 | 2 | 6 | 627 | -634 | 1 | 2 | 12 | 253 | -265 | 1 | 15 | 9 | 127 | 17 | 2 | 14 | 0 | 527 | -541 | 3 | 16 | 4 | 140 | -140 |
| 0 | 2 | 8 | 337 | -407 | 1 | 3 | 0 | 129 | -111 | 1 | 17 | 0 | 333 | 334 | 2 | 14 | 2 | 231 | -211 | 3 | 17 | 0 | 223 | -213 |
| 0 | 2 | 14 | 140 | 127 | 1 | 3 | 1 | 81 | -76 | 1 | 17 | 6 | 211 | -204 | 2 | 14 | 5 | 128 | -135 | 3 | 17 | 6 | 228 | 212 |
| 0 | 3 | 2 | 2819 | -3290 | 1 | 3 | 2 | 1267 | 1244 | 1 | 18 | 2 | 202 | -172 | 2 | 14 | 6 | 330 | 330 | 4 | 0 | 0 | 1735 | 1566 |
| 0 | 3 | 4 | 1232 | -1217 | 1 | 3 | 3 | 402 | 362 | 1 | 18 | 4 | 126 | -94 | 2 | 14 | 8 | 149 | 127 | 4 | 0 | 2 | 1204 | 1049 |
| 0 | 3 | 6 | 314 | -317 | 1 | 3 | 4 | 176 | -169 | 1 | 19 | 0 | 348 | 349 | 2 | 15 | 2 | 141 | 145 | 4 | 0 | 4 | 513 | -474 |
| 0 | 3 | 8 | 482 | -460 | 1 | 3 | 5 | 351 | -355 | 1 | 20 | 1 | 134 | -5 | 2 | 15 | 4 | 223 | 219 | 4 | 0 | 6 | 968 | -945 |
| 0 | 3 | 10 | 667 | 649 | 1 | 3 | 6 | 1265 | -1357 | 1 | 20 | 2 | 132 | -95 | 2 | 16 | 0 | 136 | -121 | 4 | 0 | 8 | 529 | -512 |
| 0 | 4 | 0 | 951 | -1046 | 1 | 3 | 8 | 378 | -524 | 1 | 20 | 4 | 161 | -104 | 2 | 16 | 1 | 87 | 64 | 4 | 0 | 12 | 216 | 211 |
| 0 | 4 | 2 | 654 | -640 | 1 | 4 | 0 | 96 | 109 | 2 | 0 | 0 | 2217 | -2077 | 2 | 16 | 5 | 121 | -94 | 4 | 1 | 1 | 413 | -373 |
| 0 | 4 | 4 | 593 | -528 | 1 | 4 | 12 | 224 | 231 | 2 | 0 | 2 | 1444 | -1262 | 2 | 16 | 8 | 172 | -172 | 4 | 1 | 3 | 375 | -349 |
| 0 | 4 | 6 | 334 | 332 | 1 | 4 | 1 | 91 | -93 | 2 | 0 | 4 | 30 | -92 | 2 | 17 | 2 | 256 | 242 | 4 | 1 | 5 | 429 | -429 |
| 0 | 4 | 8 | 195 | 190 | 1 | 4 | 2 | 140 | 108 | 2 | 0 | 6 | 1373 | 1300 | 2 | 17 | 4 | 246 | 213 | 4 | 1 | 8 | 138 | 103 |
| 0 | 5 | 2 | 1255 | -1224 | 1 | 4 | 3 | 285 | 250 | 2 | 0 | 8 | 578 | 562 | 2 | 19 | 1 | 127 | 35 | 4 | 1 | 9 | 156 | 139 |
| 0 | 5 | 4 | 973 | -861 | 1 | 4 | 4 | 549 | -563 | 2 | 0 | 12 | 292 | -279 | 2 | 19 | 2 | 124 | 108 | 4 | 1 | 10 | 184 | 194 |
| 0 | 5 | 6 | 197 | -203 | 1 | 4 | 5 | 115 | 115 | 2 | 1 | 1 | 363 | 339 | 2 | 20 | 0 | 188 | 162 | 4 | 2 | 0 | 576 | 575 |
| 0 | 5 | 8 | 335 | -329 | 1 | 4 | 6 | 185 | -180 | 2 | 1 | 2 | 2029 | 1800 | 3 | 0 | 2 | 218 | -162 | 4 | 2 | 2 | 643 | -615 |
| 0 | 5 | 10 | 297 | 276 | 1 | 4 | 7 | 112 | -77 | 2 | 1 | 3 | 113 | -61 | 3 | 0 | 4 | 1426 | -1278 | 4 | 2 | 6 | 627 | -624 |
| 0 | 5 | 12 | 133 | 109 | 1 | 4 | 8 | 162 | 176 | 2 | 1 | 4 | 452 | 445 | 3 | 0 | 6 | 384 | -378 | 4 | 2 | 7 | 168 | 163 |
| 0 | 6 | 0 | 1530 | -1819 | 1 | 5 | 0 | 1262 | 1301 | 2 | 2 | 0 | 1806 | -1971 | 3 | 0 | 8 | 470 | 469 | 4 | 2 | 8 | 284 | -268 |
| 0 | 6 | 2 | 877 | -891 | 1 | 5 | 1 | 418 | -386 | 2 | 2 | 1 | 347 | 345 | 3 | 0 | 10 | 487 | 461 | 4 | 2 | 9 | 136 | 74 |
| 0 | 6 | 4 | 189 | 190 | 1 | 5 | 2 | 1100 | 1051 | 2 | 2 | 2 | 838 | -778 | 3 | 1 | 0 | 959 | -912 | 4 | 3 | 1 | 495 | -475 |
| 0 | 6 | 6 | 922 | 899 | 1 | 5 | 3 | 182 | -164 | 2 | 2 | 3 | 536 | -495 | 3 | 1 | 2 | 627 | 560 | 4 | 3 | 2 | 1219 | -1159 |
| 0 | 6 | 8 | 555 | 541 | 1 | 5 | 4 | 477 | -484 | 2 | 2 | 4 | 707 | 684 | 3 | 1 | 2 | 871 | -764 | 4 | 3 | 4 | 1167 | -1128 |
| 0 | 6 | 12 | 187 | -225 | 1 | 5 | 5 | 482 | 507 | 2 | 2 | 5 | 256 | 261 | 3 | 1 | 4 | 477 | 369 | 4 | 3 | 8 | 339 | 339 |
| 0 | 7 | 2 | 673 | 676 | 1 | 5 | 6 | 771 | -821 | 2 | 2 | 6 | 549 | 569 | 3 | 1 | 5 | 550 | 549 | 4 | 3 | 10 | 437 | 417 |
| 0 | 7 | 4 | 331 | 349 | 1 | 5 | 7 | 70 | 83 | 2 | 2 | 8 | 460 | 493 | 3 | 1 | 6 | 592 | 593 | 4 | 4 | 0 | 258 | -249 |
| 0 | 7 | 6 | 142 | -124 | 1 | 5 | 8 | 394 | -387 | 2 | 2 | 12 | 200 | -144 | 3 | 1 | 2 | 1269 | -1218 | 4 | 4 | 2 | 643 | -623 |
| 0 | 7 | 8 | 144 | -124 | 1 | 5 | 9 | 139 | -132 | 2 | 3 | 1 | 559 | 516 | 3 | 2 | 3 | 605 | 580 | 4 | 4 | 5 | 361 | 364 |
| 0 | 8 | 0 | 1165 | -1286 | 1 | 5 | 12 | 131 | 156 | 2 | 3 | 2 | 1495 | 1498 | 3 | 2 | 4 | 763 | -747 | 4 | 4 | 7 | 180 | 197 |
| 0 | 8 | 2 | 518 | -519 | 1 | 6 | 1 | 460 | 429 | 2 | 3 | 3 | 328 | 310 | 3 | 3 | 0 | 2060 | -1942 | 4 | 4 | 8 | 145 | 131 |
| 0 | 8 | 4 | 272 | 254 | 1 | 6 | 2 | 1290 | -1273 | 2 | 3 | 4 | 1595 | 1619 | 3 | 3 | 1 | 342 | 312 | 4 | 4 | 11 | 155 | -90 |
| 0 | 8 | 6 | 721 | 701 | 1 | 6 | 3 | 230 | -217 | 2 | 3 | 5 | 238 | 251 | 3 | 3 | 2 | 1919 | -1773 | 4 | 5 | 2 | 643 | -616 |
| 0 | 8 | 8 | 329 | 305 | 1 | 6 | 4 | 1158 | -1113 | 2 | 3 | 8 | 389 | -439 | 3 | 3 | 4 | 443 | 421 | 4 | 5 | 3 | 275 | 257 |
| 0 | 9 | 2 | 538 | 551 | 1 | 6 | 5 | 96 | -79 | 2 | 3 | 10 | 418 | -463 | 3 | 3 | 5 | 251 | -243 | 4 | 5 | 4 | 1170 | -1146 |
| 0 | 9 | 4 | 825 | 798 | 1 | 6 | 6 | 346 | -340 | 2 | 3 | 12 | 143 | -165 | 3 | 3 | 6 | 1047 | 1062 | 4 | 5 | 7 | 141 | 130 |
| 0 | 9 | 6 | 258 | 243 | 1 | 6 | 7 | 122 | 115 | 2 | 4 | 0 | 1136 | 1203 | 3 | 3 | 8 | 495 | 508 | 4 | 5 | 8 | 355 | 366 |
| 0 | 9 | 8 | 265 | -246 | 1 | 6 | 8 | 385 | 381 | 2 | 4 | 1 | 166 | 157 | 3 | 3 | 12 | 246 | -187 | 4 | 5 | 9 | 132 | 142 |
| 0 | 9 | 10 | 243 | 242 | 1 | 6 | 10 | 418 | 415 | 2 | 4 | 2 | 243 | 228 | 3 | 4 | 1 | 496 | 449 | 4 | 5 | 10 | 95 | 166 |
| 0 | 9 | 12 | 122 | -116 | 1 | 6 | 12 | 118 | 116 | 2 | 4 | 4 | 371 | -380 | 3 | 4 | 2 | 503 | 476 | 4 | 6 | 0 | 1223 | -1239 |
| 0 | 10 | 0 | 64 | 59 | 1 | 7 | 0 | 160 | 153 | 2 | 4 | 8 | 274 | -322 | 3 | 4 | 3 | 477 | 483 | 4 | 6 | 2 | 564 | -557 |
| 0 | 10 | 2 | 112 | 114 | 1 | 7 | 1 | 83 | 67 | 2 | 5 | 1 | 74 | -63 | 3 | 4 | 4 | 434 | 437 | 4 | 6 | 4 | 222 | 222 |
| 0 | 10 | 4 | 241 | -241 | 1 | 7 | 2 | 177 | -172 | 2 | 5 | 2 | 785 | 791 | 3 | 5 | 2 | 292 | 289 | 4 | 6 | 6 | 577 | 586 |
| 0 | 10 | 6 | 149 | 128 | 1 | 7 | 3 | 60 | -36 | 2 | 5 | 3 | 131 | -130 | 3 | 5 | 4 | 730 | -617 | 4 | 6 | 7 | 91 | 88 |
| 0 | 11 | 2 | 439 | 433 | 1 | 7 | 4 | 99 | -105 | 2 | 5 | 4 | 985 | 984 | 3 | 5 | 0 | 1842 | -1832 | 4 | 6 | 8 | 482 | 490 |
| 0 | 11 | 4 | 713 | 711 | 1 | 7 | 6 | 167 | 159 | 2 | 5 | 6 | 249 | 259 | 3 | 5 | 1 | 284 | 271 | 4 | 6 | 9 | 100 | -62 |
| 0 | 11 | 6 | 173 | 147 | 1 | 8 | 1 | 94 | 77 | 2 | 5 | 8 | 283 | -336 | 3 | 5 | 2 | 259 | -259 | 4 | 6 | 12 | 150 | -166 |
| 0 | 11 | 8 | 247 | -245 | 1 | 8 | 2 | 1647 | -1660 | 2 | 5 | 10 | 213 | -307 | 3 | 5 | 4 | 405 | 411 | 4 | 7 | 3 | 317 | 320 |
| 0 | 11 | 10 | 209 | 189 | 1 | 8 | 3 | 229 | 217 | 2 | 6 | 0 | 1696 | 1775 | 3 | 5 | 6 | 310 | 332 | 4 | 7 | 5 | 398 | 395 |
| 0 | 12 | 0 | 270 | 260 | 1 | 8 | 4 | 1004 | -981 | 2 | 6 | 1 | 414 | 414 | 3 | 5 | 8 | 485 | 515 | 4 | 7 | 7 | 276 | -294 |
| 0 | 12 | 2 | 449 | -452 | 1 | 8 | 6 | 119 | -71 | 2 | 6 | 2 | 960 | 951 | 3 | 5 | 12 | 205 | -182 | 4 | 7 | 12 | 162 | -37 |
| 0 | 12 | 4 | 147 | -130 | 1 | 8 | 8 | 310 | 293 | 2 | 6 | 3 | 233 | -225 | 3 | 6 | 1 | 314 | -284 | 4 | 8 | 0 | 722 | -755 |
| 0 | 12 | 6 | 337 | -321 | 1 | 8 | 10 | 344 | 314 | 2 | 6 | 4 | 514 | -524 | 3 | 6 | 2 | 1026 | 1008 | 4 | 8 | 1 | 271 | 262 |
| 0 | 12 | 8 | 244 | -215 | 1 | 8 | 12 | 121 | 69 | 2 | 6 | 6 | 84 | -905 | 3 | 6 | 4 | 1195 | 1224 | 4 | 8 | 2 | 759 | -743 |
| 0 | 13 | 2 | 274 | 267 | 1 | 9 | 0 | 1211 | - | | | | | | | | | | | | | | | |

Table 1. Continued.

| <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c | | | | | | | |
|----------|----------|----------|-----------------------|-----------------------|----------|----------|----------|-----------------------|-----------------------|----------|----------|----------|-----------------------|-----------------------|----------|----------|----------|-----------------------|-----------------------|---|----|----|-----|------|------|------|
| 4 | 14 | 6 | 259 | -235 | 5 | 9 | 8 | 201 | 244 | 6 | 7 | 3 | 244 | -241 | 7 | 6 | 10 | 235 | -165 | 8 | 9 | 2 | 213 | 201 | | |
| 4 | 14 | 8 | 162 | -144 | 5 | 10 | 1 | 149 | 446 | 6 | 7 | 5 | 234 | -226 | 7 | 7 | 0 | 199 | 71 | 8 | 9 | 6 | 298 | 291 | | |
| 4 | 15 | 2 | 256 | -240 | 5 | 10 | 3 | 222 | 207 | 6 | 7 | 6 | 137 | -104 | 7 | 7 | 1 | 389 | 395 | 8 | 10 | 1 | 152 | 150 | | |
| 4 | 15 | 4 | 225 | -205 | 5 | 10 | 4 | 94 | 43 | 6 | 7 | 7 | 115 | 109 | 7 | 7 | 2 | 105 | 13 | 8 | 10 | 6 | 160 | 52 | | |
| 4 | 17 | 2 | 244 | -219 | 5 | 11 | 0 | 414 | -476 | 6 | 7 | 9 | 154 | 112 | 7 | 7 | 5 | 282 | -283 | 8 | 10 | 7 | 204 | -157 | | |
| 4 | 17 | 4 | 194 | -113 | 5 | 11 | 1 | 116 | 86 | 6 | 8 | 0 | 52 | 748 | 7 | 7 | 7 | 217 | -194 | 8 | 11 | 1 | 162 | -150 | | |
| 4 | 18 | 0 | 194 | -173 | 5 | 11 | 2 | 305 | -311 | 6 | 8 | 1 | 254 | -274 | 7 | 8 | 1 | 133 | -122 | 8 | 11 | 2 | 253 | 253 | | |
| 4 | 20 | 0 | 185 | -156 | 5 | 11 | 3 | 144 | -143 | 6 | 8 | 2 | 283 | 305 | 7 | 8 | 2 | 237 | 248 | 8 | 11 | 3 | 157 | -153 | | |
| 5 | 0 | 2 | 1532 | 1544 | 5 | 11 | 4 | 148 | -143 | 6 | 8 | 4 | 186 | -178 | 7 | 8 | 3 | 229 | -199 | 8 | 11 | 4 | 221 | 198 | | |
| 5 | 0 | 4 | 1223 | 1131 | 5 | 11 | 5 | 150 | -143 | 6 | 8 | 5 | 202 | -195 | 7 | 8 | 4 | 407 | 408 | 8 | 11 | 6 | 177 | 100 | | |
| 5 | 0 | 6 | 252 | 220 | 5 | 11 | 6 | 287 | 266 | 6 | 8 | 6 | 317 | -325 | 7 | 8 | 6 | 194 | 101 | 8 | 12 | 0 | 255 | 210 | | |
| 5 | 0 | 8 | 520 | -457 | 5 | 11 | 8 | 558 | 223 | 6 | 8 | 7 | 153 | 141 | 7 | 8 | 8 | 195 | -112 | 8 | 13 | 3 | 186 | -112 | | |
| 5 | 0 | 10 | 425 | -379 | 5 | 11 | 8 | 250 | 236 | 6 | 8 | 8 | 321 | -294 | 7 | 9 | 0 | 550 | 566 | 8 | 14 | 2 | 180 | 176 | | |
| 5 | 1 | 0 | 533 | 560 | 5 | 12 | 3 | 115 | 68 | 6 | 9 | 1 | 200 | 222 | 7 | 9 | 1 | 198 | 212 | 8 | 0 | 2 | 556 | 559 | | |
| 5 | 1 | 1 | 383 | 401 | 5 | 12 | 4 | 279 | 271 | 6 | 9 | 2 | 416 | -450 | 7 | 9 | 2 | 230 | 229 | 8 | 0 | 4 | 158 | 246 | | |
| 5 | 1 | 2 | 403 | 383 | 5 | 12 | 6 | 155 | 73 | 6 | 9 | 3 | 100 | -86 | 7 | 9 | 3 | 146 | -146 | 8 | 0 | 6 | 166 | 192 | | |
| 5 | 1 | 3 | 80 | 240 | 5 | 12 | 6 | 796 | -191 | 6 | 9 | 3 | 509 | -504 | 7 | 9 | 4 | 139 | -114 | 8 | 0 | 1 | 147 | 274 | | |
| 5 | 1 | 4 | 304 | -294 | 5 | 13 | 1 | 218 | 224 | 6 | 9 | 5 | 137 | -140 | 7 | 9 | 6 | 332 | -324 | 8 | 0 | 2 | 121 | 102 | | |
| 5 | 1 | 6 | 536 | -494 | 5 | 13 | 3 | 120 | -73 | 6 | 9 | 6 | 127 | -79 | 7 | 10 | 1 | 188 | -191 | 8 | 0 | 3 | 136 | 108 | | |
| 5 | 1 | 7 | 270 | -268 | 5 | 13 | 6 | 139 | 98 | 6 | 9 | 8 | 168 | 154 | 7 | 10 | 3 | 314 | -310 | 8 | 0 | 5 | 250 | -250 | | |
| 5 | 2 | 1 | 319 | -340 | 5 | 14 | 2 | 201 | 205 | 6 | 9 | 10 | 196 | 158 | 7 | 10 | 4 | 104 | 120 | 8 | 0 | 2 | 291 | -298 | | |
| 5 | 2 | 2 | 482 | 244 | 5 | 14 | 4 | 281 | 259 | 6 | 10 | 0 | 197 | 224 | 7 | 11 | 0 | 272 | 279 | 8 | 0 | 2 | 281 | 311 | | |
| 5 | 2 | 4 | 271 | -521 | 5 | 14 | 4 | 156 | -104 | 6 | 10 | 1 | 209 | -221 | 7 | 11 | 1 | 212 | -192 | 8 | 0 | 2 | 5 | 247 | | |
| 5 | 2 | 4 | 709 | 672 | 5 | 15 | 0 | 206 | 190 | 6 | 10 | 5 | 199 | 190 | 7 | 11 | 2 | 268 | 248 | 8 | 0 | 3 | 0 | 339 | 528 | |
| 5 | 2 | 5 | 171 | -152 | 5 | 15 | 3 | 160 | -137 | 6 | 10 | 7 | 143 | 153 | 7 | 11 | 6 | 212 | -154 | 8 | 0 | 3 | 2 | 290 | 256 | |
| 5 | 2 | 6 | 132 | 114 | 5 | 16 | 4 | 153 | 121 | 6 | 11 | 2 | 354 | -393 | 7 | 11 | 8 | 196 | -155 | 8 | 0 | 3 | 4 | 153 | -142 | |
| 5 | 2 | 7 | 98 | 89 | 5 | 17 | 2 | 182 | 136 | 6 | 11 | 3 | 130 | 124 | 7 | 12 | 2 | 194 | -196 | 8 | 0 | 3 | 5 | 155 | -81 | |
| 5 | 2 | 8 | 208 | -182 | 6 | 0 | 0 | 940 | -1033 | 6 | 11 | 4 | 370 | -375 | 7 | 12 | 3 | 152 | -137 | 8 | 0 | 3 | 6 | 174 | -178 | |
| 5 | 2 | 9 | 242 | 211 | 6 | 0 | 0 | 543 | -505 | 6 | 12 | 0 | 378 | -432 | 7 | 12 | 4 | 232 | -222 | 8 | 0 | 3 | 8 | 272 | 279 | |
| 5 | 2 | 10 | 235 | -188 | 6 | 0 | 4 | 307 | 278 | 6 | 12 | 2 | 162 | -150 | 7 | 13 | 1 | 261 | -222 | 8 | 0 | 4 | 3 | 364 | -352 | |
| 5 | 3 | 0 | 1460 | 1686 | 6 | 0 | 6 | 431 | 420 | 6 | 12 | 5 | 160 | 50 | 7 | 13 | 5 | 184 | 127 | 8 | 0 | 4 | 9 | 182 | 171 | |
| 5 | 3 | 1 | 339 | 353 | 6 | 0 | 8 | 567 | 505 | 6 | 12 | 6 | 273 | 266 | 7 | 13 | 6 | 170 | -130 | 8 | 0 | 5 | 0 | 394 | 384 | |
| 5 | 3 | 2 | 756 | 767 | 6 | 0 | 12 | 197 | -129 | 6 | 13 | 2 | 136 | -129 | 7 | 14 | 1 | 149 | 110 | 8 | 0 | 5 | 1 | 248 | -200 | |
| 5 | 3 | 3 | 426 | -421 | 6 | 1 | 1 | 304 | 325 | 6 | 14 | 0 | 295 | -283 | 7 | 14 | 2 | 246 | -221 | 8 | 0 | 5 | 2 | 178 | -603 | |
| 5 | 3 | 4 | 556 | -524 | 6 | 1 | 2 | 373 | 369 | 6 | 14 | 2 | 263 | -238 | 7 | 14 | 4 | 213 | -150 | 8 | 0 | 5 | 5 | 241 | 205 | |
| 5 | 3 | 5 | 89 | 67 | 6 | 1 | 3 | 503 | 471 | 6 | 14 | 4 | 167 | 153 | 7 | 15 | 0 | 187 | -172 | 8 | 0 | 5 | 6 | 257 | -261 | |
| 5 | 3 | 6 | 788 | -734 | 6 | 1 | 4 | 457 | 410 | 6 | 14 | 6 | 155 | 174 | 7 | 17 | 0 | 162 | -137 | 8 | 0 | 6 | 2 | 262 | -241 | |
| 5 | 3 | 8 | 541 | -498 | 6 | 1 | 5 | 246 | 195 | 6 | 14 | 8 | 158 | 117 | 8 | 0 | 0 | 679 | 711 | 8 | 0 | 6 | 4 | 318 | -281 | |
| 5 | 4 | 1 | 271 | -253 | 6 | 1 | 7 | 116 | -108 | 6 | 15 | 4 | 188 | 172 | 8 | 0 | 2 | 380 | -472 | 8 | 0 | 6 | 6 | 145 | -134 | |
| 5 | 4 | 2 | 247 | -245 | 6 | 1 | 8 | 149 | -132 | 6 | 16 | 2 | 191 | 154 | 8 | 0 | 4 | 220 | -291 | 8 | 0 | 7 | 1 | 100 | -291 | |
| 5 | 4 | 3 | 264 | -266 | 6 | 1 | 9 | 203 | -182 | 6 | 17 | 4 | 199 | 142 | 8 | 0 | 6 | 267 | -358 | 8 | 0 | 7 | 4 | 228 | 189 | |
| 5 | 4 | 4 | 564 | -532 | 6 | 1 | 10 | 171 | -138 | 7 | 0 | 2 | 381 | -363 | 8 | 0 | 8 | 265 | -277 | 8 | 0 | 7 | 1 | 193 | 165 | |
| 5 | 4 | 5 | 269 | -266 | 6 | 2 | 0 | 779 | -877 | 7 | 0 | 4 | 907 | -920 | 8 | 0 | 1 | 327 | -339 | 8 | 0 | 8 | 2 | 299 | -291 | |
| 5 | 4 | 6 | 147 | 134 | 6 | 2 | 1 | 552 | 596 | 7 | 0 | 6 | 204 | -181 | 8 | 1 | 2 | 163 | -150 | 8 | 0 | 8 | 3 | 181 | -219 | |
| 5 | 5 | 0 | 691 | 774 | 6 | 2 | 2 | 267 | -246 | 7 | 0 | 8 | 320 | 273 | 8 | 1 | 3 | 448 | -430 | 8 | 0 | 8 | 4 | 320 | -304 | |
| 5 | 5 | 1 | 391 | -420 | 6 | 2 | 4 | 185 | 139 | 7 | 0 | 10 | 177 | 183 | 8 | 1 | 4 | 250 | -276 | 8 | 0 | 9 | 0 | 291 | -274 | |
| 5 | 5 | 2 | 455 | -465 | 6 | 2 | 5 | 434 | -420 | 7 | 1 | 0 | 828 | -852 | 8 | 1 | 5 | 126 | -140 | 8 | 0 | 10 | 3 | 288 | 276 | |
| 5 | 5 | 4 | 193 | -182 | 6 | 2 | 6 | 459 | -435 | 7 | 1 | 1 | 341 | -350 | 8 | 2 | 0 | 476 | -509 | 8 | 0 | 11 | 0 | 182 | -198 | |
| 5 | 5 | 5 | 287 | -278 | 6 | 2 | 7 | 293 | -209 | 7 | 1 | 2 | 136 | 94 | 8 | 2 | 1 | 520 | -508 | 8 | 0 | 11 | 2 | 202 | -219 | |
| 5 | 5 | 6 | 447 | -518 | 6 | 2 | 8 | 228 | -189 | 7 | 1 | 3 | 270 | 274 | 8 | 2 | 2 | 129 | -144 | 8 | 0 | 11 | 4 | 194 | 178 | |
| 5 | 5 | 7 | 252 | -257 | 6 | 2 | 12 | 179 | -107 | 7 | 1 | 6 | 280 | 264 | 8 | 2 | 3 | 622 | -577 | 8 | 0 | 12 | 2 | 167 | 136 | |
| 5 | 5 | 8 | 256 | -221 | 6 | 3 | 1 | 247 | -254 | 7 | 1 | 7 | 257 | 247 | 8 | 2 | 5 | 154 | 162 | 8 | 0 | 13 | 1 | 164 | 176 | |
| 5 | 5 | 9 | 105 | -54 | 6 | 3 | 2 | 678 | 726 | 7 | 1 | 8 | 188 | 170 | 8 | 2 | 6 | 280 | -272 | 8 | 0 | 13 | 0 | 0 | 238 | -274 |
| 5 | 5 | 10 | 144 | -23 | 6 | 3 | 3 | 174 | 181 | 7 | 2 | 2 | 534 | -546 | 8 | 2 | 7 | 205 | -199 | 8 | 0 | 14 | 0 | 2 | 344 | -356 |
| 5 | 6 | 1 | 250 | -222 | 6 | 3 | 4 | 730 | 708 | 7 | 2 | 3 | 304 | -301 | 8 | 2 | 8 | 152 | -126 | 8 | 0 | 14 | 0 | 6 | 259 | 307 |
| 5 | 6 | 2 | 831 | -874 | 6 | 3 | 5 | 110 | 195 | 7 | 2 | 4 | 399 | -387 | 8 | 2 | 9 | 622 | -566 | 8 | 0 | 14 | 1 | 1 | 187 | 201 |
| 5 | 6 | 3 | 231 | -217 | 6 | 3 | 6 | 267 | 253 | 7 | 2 | 5 | 291 | 309 | 8 | 3 | 3 | 130 | 105 | 8 | 0 | 14 | 1 | 3 | 291 | 308 |
| 5 | 6 | 4 | 697 | -686 | 6 | 3 | 7 | 152 | -135 | 7 | 2 | 7 | 142 | -109 | 8 | 3 | 4 | 506 | -478 | 8 | 0 | 14 | 1 | 4 | 167 | 167 |
| 5 | 6 | 5 | 211 | 201 | 6 | 3 | 8 | 265 | -218 | 7 | 2 | 10 | 224 | 192 | 8 | 3 | 6 | 153 | -133 | 8 | 0 | 14 | 2 | 0 | 237 | -245 |
| 5 | 6 | 6 | 231 | -222 | 6 | 3 | 10 | 253 | -271 | 7 | 3 | 0 | 502 | -522 | 8 | 3 | 8 | 170 | -169 | 8 | 0 | 14 | 2 | 1 | 254 | -315 |
| 5 | 6 | 7 | 120 | -91 | 6 | 3 | 10 | 330 | 349 | 7 | 3 | 1 | 97 | -82 | 8 | 4 | 0 | 195 | -174 | 8 | 0 | 14 | 2 | 5 | 209 | -215 |
| 5 | 6 | 8 | 243 | 227 | 6 | 4 | 1 | 319 | 349 | 7 | 3 | 2 | 682 | -679 | 8 | 4 | 1 | 433 | -438 | 8 | 0 | 14 | 3 | 2 | 246 | 260 |
| 5 | 6 | 10 | 305 | 306 | 6 | 4 | 3 | 92 | 32 | 7 | 3 | 4 | 224 | 203 | 8 | 4 | 2 | 155 | -93 | 8 | 0 | 14 | 3 | 4 | 360 | 347 |
| 5 | 7 | 0 | 189 | -191 | 6 | 4 | 5 | 216 | -218 | 7 | 3 | 6 | 581 | 545 | 8 | 4 | 5 | 415 | 375 | 8 | 0 | 14 | 4 | 1 | 269 | 281 |
| 5 | 7 | 1 | 405 | -441 | 6 | 4 | 7 | 250 | -230 | 7 | 3 | 8 | 280 | 289 | 8 | 4 | 6 | 216 | 175 | 8 | 0 | 14 | 4 | 2 | 181 | -244 |
| 5 | 7 | 3 | 185 | -219 | 6 | 4 | 8 | 156 | -103 | 7 | 4 | 1 | 295 | 300 | 8 | 4 | 7 | 231 | -219 | 8 | 0 | 14 | 6 | 0 | 173 | |

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^3$). 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 | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> ₁₁ | <i>B</i> ₂₂ | <i>B</i> ₃₃ | <i>B</i> ₁₂ | <i>B</i> ₁₃ | <i>B</i> ₂₃ |
|-----------------|----------|----------|----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Rb ⁺ | 26282 | 57479 | -7613 | 872 | 520 | 984 | 189 | -268 | 35 |
| | 10 | 6 | 8 | 15 | 5 | 12 | 15 | 24 | 13 |
| C | 18255 | 28753 | 24296 | 532 | 253 | 754 | 112 | -8 | -190 |
| | 96 | 52 | 90 | 110 | 32 | 102 | 113 | 195 | 101 |
| N1 | 21175 | 37674 | 16815 | 624 | 269 | 807 | 32 | -408 | -185 |
| | 82 | 48 | 69 | 116 | 31 | 89 | 98 | 172 | 90 |
| N2 | 3146 | 26859 | 32145 | 687 | 347 | 820 | 35 | 61 | 27 |
| | 89 | 43 | 78 | 112 | 47 | 87 | 100 | 178 | 94 |
| O11 | 35135 | 38480 | 9980 | 905 | 308 | 1451 | -204 | 663 | 324 |
| | 77 | 39 | 79 | 104 | 30 | 107 | 93 | 188 | 105 |
| O12 | 10828 | 44887 | 17426 | 1134 | 271 | 1434 | 292 | -177 | -126 |
| | 92 | 39 | 67 | 114 | 30 | 106 | 100 | 179 | 86 |
| O21 | -9503 | 32704 | 31919 | 812 | 736 | 1518 | 797 | 531 | 487 |
| | 91 | 54 | 76 | 113 | 46 | 117 | 127 | 190 | 115 |
| O22 | 2466 | 18993 | 39448 | 964 | 531 | 1350 | 5 | 539 | 678 |
| | 79 | 46 | 77 | 110 | 43 | 101 | 104 | 198 | 117 |

Table 3. The root mean square amplitudes of vibration ($\overline{u^2}$)^{1/2} (Å) and *B*-values (Å²) along the principal axes given by the components of a unit vector in fractional coordinates ($\times 10^3$).

| Atom | ($\overline{u^2}$) ^{1/2} | <i>B</i> | <i>e</i> _{<i>x</i>} | <i>e</i> _{<i>y</i>} | <i>e</i> _{<i>z</i>} |
|-----------------|-------------------------------------|----------|------------------------------|------------------------------|------------------------------|
| Rb ⁺ | .219 | 3.80 | 28 | 73 | 0 |
| | .201 | 3.19 | -37 | 5 | 108 |
| | .154 | 1.86 | 121 | -16 | 33 |
| C | .182 | 2.62 | 12 | 38 | -97 |
| | .145 | 1.65 | 56 | 57 | 55 |
| | .121 | 1.16 | -116 | 31 | 17 |
| N1 | .193 | 2.94 | 44 | 29 | -97 |
| | .149 | 1.76 | -43 | 68 | 31 |
| | .124 | 1.22 | 114 | 14 | 49 |
| N2 | .182 | 2.61 | 14 | 36 | 99 |
| | .176 | 2.44 | 4 | 66 | -54 |
| | .143 | 1.62 | -129 | 6 | 9 |
| O11 | .251 | 4.97 | 35 | 16 | 106 |
| | .181 | 2.59 | -87 | 56 | 2 |
| | .129 | 1.32 | 90 | 47 | -39 |
| O12 | .241 | 4.57 | 22 | 11 | -110 |
| | .193 | 2.94 | 112 | 34 | 25 |
| | .142 | 1.59 | -61 | 66 | 6 |
| O21 | .293 | 6.80 | 44 | 57 | 62 |
| | .222 | 3.88 | 18 | 40 | -94 |
| | .125 | 1.24 | -121 | 27 | 8 |
| O22 | .269 | 5.71 | 21 | 47 | 86 |
| | .187 | 2.77 | 81 | -50 | 47 |
| | .152 | 1.81 | 100 | 30 | -57 |

Table 4. Bond distances, bond angles, and *intra*-molecular contacts of the anion. Atoms related by the two-fold rotation axis are marked by a prime.

| Bond distances (Å) | | Bond angles (°) | |
|--------------------------------------|-------|-----------------|-------|
| C-C' | 1.444 | C'-C-N1 | 118.8 |
| C-N1 | 1.381 | C'-C-N2 | 118.7 |
| C-N2 | 1.378 | N1-C-N2 | 122.5 |
| N1-O11 | 1.238 | C-N1-O11 | 116.7 |
| N1-O12 | 1.251 | C-N1-O12 | 122.7 |
| N2-O21 | 1.249 | O11-N1-O12 | 120.5 |
| N2-O22 | 1.234 | C-N2-O21 | 122.4 |
| | | C-N2-O22 | 117.1 |
| | | O21-N2-O22 | 120.5 |
| <i>Intra</i> -molecular contacts (Å) | | | |
| O12...O21 | 2.60 | | |
| O11...O22' | 2.94 | | |
| O11...N2' | 2.97 | | |
| O11...C' | 2.64 | | |

Table 5. Coordination distances of the rubidium ion.

| Atom | Equiv. pos. | No. | (Å) |
|------|-------------------------------------|-----|------|
| O11 | x, y, z | 1 | 3.05 |
| O11 | $1-x, 1-y, -z$ | 2 | 3.03 |
| O12 | | 1 | 3.02 |
| O12 | $-x, 1-y, -z$ | 3 | 3.00 |
| O12 | $\frac{1}{2}-x, y, -\frac{1}{2}+z$ | 4 | 2.95 |
| O21 | | 3 | 2.83 |
| O21 | $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$ | 5 | 2.84 |
| O22 | $-x, \frac{1}{2}+y, \frac{1}{2}-z$ | 6 | 3.14 |

tensors are presented in Table 3. Bond distances and angles and the numbering of atoms of the anion may be found in Fig. 1 and Table 4. The estimated standard deviations calculated from the correlation matrix of the last least squares refinement cycle are 0.009, 0.010, and 0.014 Å for N-O, C-N, and C-C bonds, respectively, and 0.7° or less for the bond angles. Coordination distances of the rubidium ion is given in Table 5, and in Fig. 2 anions and surrounding cations are shown.

The r.m.s. discrepancies between "observed" atomic vibration parameters and those calculated for a rigid-body model are 0.0048 Å² for the anion (maintaining the two-fold symmetry) and 0.0031 Å² for the C-C(NO₂)₂ group. This may indicate that the C(NO₂)₂ groups are fairly rigid, but this conclusion must be regarded with caution because of the experimental difficulties concerning the data collection.

DISCUSSION

The anion may be described as an RC(NO₂)₂⁻ anion with an essentially planar C(NO₂)₂⁻ group having the group R, namely the other C(NO₂)₂⁻, twisted 68° from a planar conformation. In the potassium salt the twist angle is 63°.

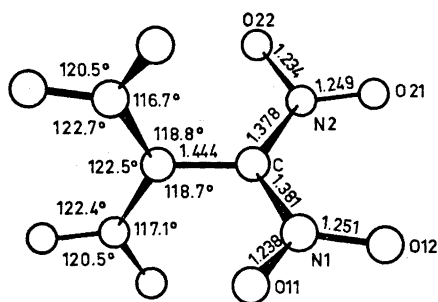


Fig. 1. Bond distances and bond angles of the anion.

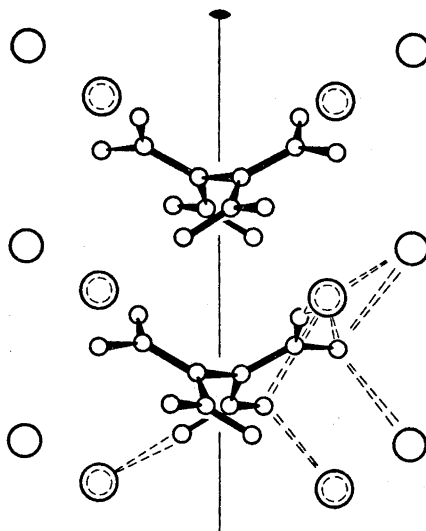


Fig. 2. A schematic drawing of the structure as viewed along a . Contacts between oxygen atoms (of one asymmetric unit) and cations are indicated by broken lines.

The double bond character of the carbon carbon bond is small, the overlap integral being less than half the value for a coplanar arrangement. The C-C bond length (1.444 Å) is not significantly different from that of normal sp^2-sp^2 C-C single bonds and more accurate investigations are necessary to decide whether the apparent shortening of the bond is real or not.

The bond distances and angles of the anion (Fig. 1) are consistent with an ideal model having D_2 symmetry. The planar groups of one carbon atom are propeller twisted. The planes through N1, O11, O12 and through N2, O21, O22 form angles of 4.1° and 6.1° with the plane through C, N1, N2. The deviations of the oxygen atoms from the C1, N1, N2 plane are -0.018 , 0.086 , -0.118 , and 0.112 Å for O11, O12, O21, and O22, respectively. This shows that whereas one nitro group (N2) is twisted about the carbon nitrogen bond the other (N1) has an additional slight bend. The D_2 symmetry is thus destroyed. The carbon atom is coplanar with its neighbours, the deviation from the plane through N1, N2, and C' being 0.014 Å. The conformation of the anion in the crystal is determined by coordination effects as well as intramolecular repulsions. The shortest contacts between the C(NO₂)₂ groups of an anion (Table 4) are somewhat longer than van der Waals contact distance and the twist about the central bond may be influenced by the coordination.

The cation is coordinated to eight oxygen atoms of six different anions in an irregular arrangement (Table 5). The anions situated on a two-fold symmetry axis are surrounded by cations forming a hexagon in the projection along c .¹⁴ The same arrangement as viewed along a may be seen in Fig. 2; the coordina-

Table 6. Structural data for several $R-C(NO_2)_2^-$ carbanions. Mean values are given for C-N and N-O bond lengths. The value for the C-N-O angle is the mean value of C-N1-O12 and C-N2-O21. O12...O21 contacts, the twist angle for planar groups (Tw. a.), and the e.s.d.'s in bond lengths are also quoted.

| R | Cation | Ref. | C-N | N-O | N-C-N | C-N-O | O...O | Tw. a. | e.s.d. |
|---|--|---------|-------|-------|-------|-------|-------|--------|--------|
| -CN | Rb ⁺ | 17 | 1.377 | 1.240 | 125.2 | 121.5 | 2.62 | | 0.007 |
| -CN | K ⁺ | 18 | 1.394 | 1.238 | 123.7 | 122.5 | 2.66 | | 0.004 |
| -CH=CH-CONH ₂ | K ⁺ | 13 | 1.389 | 1.248 | 120.0 | 122.5 | 2.51 | 0 | 0.009 |
| -NO ₂ | N ₂ H ₅ ⁺ | 12 | 1.391 | 1.231 | 124.3 | 120.4 | 2.59 | 41 | 0.005 |
| -NO ₂ | N ₂ H ₅ ⁺ | 12 | 1.371 | 1.239 | 127.2 | 120.7 | 2.65 | 74 | 0.005 |
| -C(NO ₂) ₂ ⁻ | K ⁺ | 15 | 1.390 | 1.245 | 121 | 121 | 2.57 | 63 | 0.02 |
| -C(NO ₂) ₂ ⁻ | Rb ⁺ | this w. | 1.380 | 1.243 | 122.5 | 122.6 | 2.60 | 68 | 0.01 |
| -C ₆ H ₅ | K ⁺ | 10 | 1.40 | 1.275 | 120 | 124 | 2.63 | 62 | 0.02 |
| -CH ₂ Cl | K ⁺ | 16 | 1.389 | 1.256 | 119.8 | 123.6 | 2.57 | 71 | 0.006 |
| -CONH ₂ | Rb ⁺ | 11 | 1.35 | 1.255 | 123 | 123.5 | 2.61 | 79 | 0.02 |
| -CH ₂ C(NO ₂) ₂ C ₂ H ₄ COCH ₃ | Rb ⁺ | 8 | 1.37 | 1.24 | 120 | 125 | 2.57 | | 0.02 |

tion between the oxygen atoms (of one asymmetric unit) and cations is also shown.

The results of several structure determinations of 1,1-dinitrocarbanion salts are summarized in Table 6. Only three-dimensional studies with standard deviations in bond lengths of 0.02 Å or less are included, thus leaving out Refs. 3, 4, 5, 6, 7, 9, and 14. Grigor'eva *et al.* have shown ⁷ (three-dimensional data) that the structure of rubidium trinitromethanide earlier determined ³ was incorrect. This must also be the case for the structure of potassium trinitromethanide.⁵ The reported conformation of the anion appears very unlikely, as are *intra*- and *inter*-ionic oxygen oxygen contacts of 2.32, 2.31, 2.42, and 2.48 Å. The tabulated data for the cyanodinitromethanide anions are based on recent diffractometer studies in this laboratory ^{17,18} rather than those of Grigor'eva *et al.*^{7,9} The anions are all considered to be $R-C(NO_2)_2^-$ anions and are arranged according to the steric requirements of R. The anion of potassium 4,4-dinitro-2-butenamide ¹³ (R = -CH=CH-CONH₂) is essentially planar and R takes part in the charge delocalization. The twist angle values of R for the other compounds show that R plays no important part in the charge delocalization. The arithmetic mean values of the carbon nitrogen and nitrogen oxygen bond lengths are 1.382 and 1.246 Å, respectively. For the values of the bond angles of Table 6 as well as the twist angles of the nitro groups (not shown) crystal effects are of importance. This has been elegantly demonstrated by the structure determination of hydrazinium trinitromethanide,¹² where two crystallographically independent anions are present.

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