

## The Crystal Structure of Potassium *p*-Chlorophenyldinitromethanide

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The crystals are orthorhombic, space group *Pbca*, with cell dimensions  $a = 12.67_0$  Å,  $b = 20.25_5$  Å, and  $c = 7.41_5$  Å. 827 X-ray reflections recorded on an automatic four-circle diffractometer were used in full-matrix least squares refinement ( $R_w = 3.0$  %,  $R = 5.9$  %). The anion is not propeller shaped, the nitro groups being twisted in opposite directions,  $10^\circ$  and  $7^\circ$ , respectively, from a planar conformation. The twist of the phenyl group is  $71^\circ$ .

Several crystal structure investigations and conformational studies of *S*1,1-dinitro carbanions have been carried out; *cf.* Ref. 1 and references therein.

From ultraviolet absorption spectra of solutions of various  $\text{RC}(\text{NO}_2)_2^-$  salts Kamlet and Glover<sup>2</sup> concluded that the twist of the phenyl ring in phenyldinitromethanide relative to the plane through the central carbon and adjacent atoms approaches  $90^\circ$  and that the phenyl group exerts a purely inductometric effect on the charge delocalization. The  $pK$  values of Sitzman *et al.*<sup>3</sup> are consistent with this conclusion.

Electron spin resonance studies of several divalent radical anions derived from aryldinitromethanes have been carried out by Torssell *et al.*<sup>4</sup> MO-calculations of the spin densities correlated to the observed splitting constants gave a somewhat better agreement for a model with the nitro groups twisted about  $65^\circ$  from the planar conformation than for a planar model. A sample of potassium *p*-chlorophenyldinitromethanide was kindly forwarded by the latter authors.

### CRYSTAL DATA

Potassium *p*-chlorophenyldinitromethanide was crystallized from aqueous solution as yellow needle formed thin plates. The crystals belong to the orthorhombic system, and the systematic absences lead to space group *Pbca*. The cell dimensions, determined at room temperature on a manual four-circle diffractometer (CuK-radiation), and their estimated standard deviations are:

$a = 12.670(3)$  Å,  $b = 20.255(4)$  Å,  $c = 7.415(1)$  Å,  $V = 1902.8$  Å<sup>3</sup>.  $c$  is the needle axis and (010) the predominant crystal face. The unit cell contains eight formula units ( $\rho_{\text{calc}} = 1.78$  g cm<sup>-3</sup>,  $\rho_{\text{obs}} = 1.80$  g cm<sup>-3</sup>).

A crystal of dimensions  $0.25 \times 0.20 \times 0.01$  mm<sup>3</sup> was used for all X-ray measurements. About 2070 reflections with  $2\theta < 53^\circ$  were registered on an automatic four-circle diffractometer using  $\omega/2\theta$  scan technique and MoK $\alpha$  radiation (0.002'' Nb filter). 907 reflections were recorded as observed, having intensities greater than twice the standard deviations from counting statistics. A 1 % uncertainty in scaling of intensities and fluctuation in diffractometer stability was included in the standard deviations. With a cut-off value of  $2.3\sigma$  the number of observed reflections was 827. The absorption-corrected observed intensities were used in the structure determination.

The computer programs used are described in Ref. 5.

### STRUCTURE DETERMINATION

The structure was determined by the heavy atom method. A Fourier synthesis based on the K<sup>+</sup> and Cl positions ( $R = 45$  %) revealed the positions of the 13 non-hydrogen atoms. The parameters were refined by full-matrix least squares technique. Inclusion of the hydrogen atoms in the refinement did not lower the  $R_w$ -value significantly and they were eventually given coordinates corresponding to a C-H bond length of 1.05 Å and a  $B$ -value of 3.0 Å<sup>2</sup>. The final  $R_w$ - and  $R$ -values were 3.2 % and 7.0 % for the 907 reflections. When the data set consisting of 827 intensities was used  $R_w = 3.0$  % and  $R = 5.9$  % were obtained. (By further omitting the 18 reflections with  $F_o$  greater than  $2 F_c$ , the  $R$  decreased to 4.9 %.) No secondary extinction effects were observed. The weight analysis showed a slight intensity dependence for the strongest reflections indicating that a higher value for the uncertainty in scaling *etc.* might be appropriate. Atomic form factors were those of Cromer and Waber<sup>6</sup> except for hydrogen.<sup>7</sup>

A comparison between the 827 observed and calculated structure factors is given in Table 1. The final atomic parameters with estimated standard deviations are listed in Table 2. The eigenvalues of the atomic vibration tensors are presented in Table 3. Bond distances and bond angles for the anion may be found in Table 4 or in Fig. 1, which also shows the numbering of atoms. The standard deviations calculated from the correlation matrix of the last least squares refinement cycle are about 0.006 Å for C-C and C-N bonds, 0.005 Å or less for Cl-C and N-O bonds, and 0.5° or less in bond angles. The atomic deviations from two least squares planes through the anion are presented in Table 5. Coordination distances of the cation are listed in Table 6. A schematical drawing of the structure showing the packing is given in Fig. 2.

TLS calculations<sup>8</sup> seem to indicate that the anion might be regarded as a segmented rigid body, the r.m.s. discrepancies between "observed" and calculated tensor components being 0.0035 Å<sup>2</sup> and 0.0032 Å<sup>2</sup> for the C(NO<sub>2</sub>)<sub>2</sub> group and the *p*-chlorophenyl group, respectively. The corrections in bond lengths, however, are not greater than the standard deviations and have not been applied.

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

$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$
0	2	0	1220	1105	16	0	0	292	-248	7	7	1	477	-478	3	2	2	669	-666	10	10	2	229	236
0	4	0	908	912	0	2	1	203	194	7	9	1	430	-433	3	3	2	520	519	10	12	2	250	233
0	6	0	1272	-1284	0	4	1	356	360	7	11	1	335	-332	3	4	2	164	171	10	14	2	200	181
0	8	0	1584	-1645	0	6	1	582	587	7	13	1	265	-244	3	5	2	309	309	11	0	2	314	-297
0	10	0	362	-399	0	12	1	448	-438	7	14	1	146	-173	3	6	2	487	485	11	2	2	231	243
0	12	0	812	-812	0	16	1	131	-107	7	22	1	108	105	3	9	2	452	-452	11	3	2	384	-263
0	14	0	202	-225	0	18	1	372	369	8	2	1	265	-259	3	4	2	318	-323	11	4	2	405	-413
0	18	0	449	-448	1	1	1	606	-604	8	4	1	574	-571	3	9	2	460	460	11	4	2	352	-365
0	24	0	246	194	1	2	1	392	-374	8	5	1	249	-246	3	10	2	445	443	11	10	2	190	-172
2	0	0	241	238	1	3	1	1083	1062	8	8	1	205	-213	3	11	2	612	-617	11	12	2	201	178
2	1	0	252	-233	1	4	1	1046	-1044	8	11	1	176	-210	3	12	2	147	-143	11	15	2	192	146
2	2	0	1241	1227	1	5	1	168	166	8	16	1	211	149	3	13	2	341	345	12	1	2	216	228
2	3	0	613	598	1	9	1	1096	-1116	9	1	1	135	-121	3	17	2	145	115	12	3	2	340	335
2	4	0	1402	-1399	1	9	1	1096	-1116	9	4	1	733	-724	3	18	2	178	169	12	5	2	316	298
2	5	0	478	477	1	1	1	429	-442	9	5	1	366	-372	3	19	2	321	328	12	7	2	271	267
2	6	0	1625	-1637	1	9	1	529	-531	9	6	1	223	-222	4	0	2	575	-572	12	9	2	207	192
2	7	0	598	597	1	10	1	209	-213	9	7	1	269	269	4	2	2	361	366	12	15	2	192	-121
2	8	0	46	-81	1	11	1	228	-237	9	8	1	403	-392	4	2	2	620	-622	13	0	2	104	312
2	9	0	1100	-1098	1	12	1	264	-265	9	9	1	248	261	4	3	2	269	261	13	14	2	221	55
2	10	0	108	96	1	13	1	207	-192	9	10	1	174	-192	4	4	2	142	144	14	0	2	193	177
2	11	0	148	143	1	14	1	377	369	9	13	1	180	183	4	5	2	513	509	14	4	2	199	186
2	12	0	720	733	1	15	1	306	-296	9	14	1	318	277	4	6	2	253	252	14	5	2	237	-100
2	14	0	508	506	1	17	1	157	136	9	20	1	248	240	4	7	2	342	341	0	2	3	262	-168
2	15	0	617	613	1	18	1	454	453	10	1	1	252	258	4	8	2	133	142	0	4	3	214	202
2	17	0	168	139	2	2	1	272	-269	10	2	1	275	-305	4	9	2	317	324	0	6	3	757	-760
2	18	0	147	-154	2	3	1	703	-690	10	4	1	174	147	4	11	2	345	333	0	10	3	152	144
2	19	0	168	183	2	4	1	695	-687	10	4	1	268	314	4	12	2	399	413	0	14	3	318	302
2	21	0	193	452	2	5	1	209	-452	10	8	1	170	147	4	13	2	153	174	0	16	3	185	-168
4	0	0	253	-275	2	6	1	728	730	10	9	1	143	-137	4	14	2	174	144	1	1	3	996	1005
4	1	0	229	-227	2	7	1	109	-115	10	12	1	216	-214	4	17	2	177	-159	1	2	3	395	393
4	2	0	1657	-1655	2	8	1	155	-153	10	13	1	227	-252	5	0	2	871	-868	1	3	3	560	-561
4	3	0	1937	1947	2	9	1	297	300	10	16	1	214	-216	5	1	2	360	370	1	4	3	565	-554
4	4	0	1293	-1310	2	10	1	110	-128	11	1	1	201	-193	5	3	2	376	-382	1	5	3	874	188
4	5	0	1062	1083	2	11	1	202	-214	11	3	1	360	-357	5	4	2	97	98	1	6	3	138	145
4	6	0	110	-134	2	12	1	156	-122	11	4	1	431	434	5	6	2	143	-142	1	7	3	361	-362
4	7	0	344	-336	2	13	1	225	-216	11	6	1	414	423	5	8	2	409	413	1	8	3	166	-171
4	8	0	431	-424	2	14	1	566	-566	11	7	1	190	186	5	9	2	381	-385	1	9	3	348	-344
4	9	0	138	-131	2	15	1	322	322	11	8	1	294	296	5	11	2	129	81	1	11	3	524	-524
4	10	0	1317	1304	2	16	1	166	-120	11	11	1	310	285	5	13	2	215	-189	1	12	3	261	261
4	11	0	1031	-1028	2	17	1	195	41	11	16	1	224	-192	5	13	2	322	-318	1	13	3	463	-446
4	12	0	775	777	3	1	1	542	-550	12	6	1	230	248	5	14	2	178	-167	1	16	3	350	340
4	14	0	468	460	3	2	1	237	-244	12	8	1	194	188	5	19	2	166	-102	2	1	3	576	573
4	15	0	250	-219	3	3	1	763	-755	13	1	1	215	203	5	21	2	205	226	2	2	3	604	594
4	19	0	362	365	3	4	1	695	-922	13	3	1	165	168	5	12	2	433	419	2	3	3	306	-312
4	21	0	206	-172	3	5	1	353	371	13	5	1	175	111	6	2	2	411	422	2	5	3	193	195
6	0	0	1181	1182	3	6	1	444	-440	13	6	1	218	229	6	3	2	501	495	2	7	3	134	-121
6	1	0	610	617	3	8	1	329	-340	13	11	1	219	-193	6	4	2	265	256	2	8	3	478	-477
6	2	0	916	913	3	9	1	685	687	13	14	1	202	-162	6	5	2	504	509	2	9	3	96	63
6	3	0	643	650	3	10	1	151	156	14	1	1	224	-186	6	6	2	217	-210	2	11	3	275	-246
6	4	0	368	366	3	11	1	220	223	14	5	1	176	-63	6	7	2	414	409	2	12	3	297	293
6	5	0	842	841	3	12	1	128	121	15	2	1	238	-178	6	8	2	166	-197	2	13	3	163	-123
6	7	0	195	223	3	13	1	159	109	15	4	1	250	-225	6	9	2	197	181	2	15	3	206	189
6	9	0	680	-685	3	14	1	283	-316	15	6	1	305	-219	6	10	2	469	-480	2	16	3	325	343
6	10	0	135	152	3	15	1	216	200	15	8	1	258	-231	6	11	2	198	-208	2	18	3	259	-261
6	12	0	750	-750	3	16	1	358	-358	0	0	2	365	363	6	12	2	348	-336	2	24	3	216	-212
6	13	0	265	-266	3	21	1	207	-217	0	2	2	251	263	6	17	2	199	-173	3	1	3	1583	-1582
6	14	0	296	-310	4	1	1	295	-294	0	4	2	330	-332	6	22	2	211	10	3	3	254	-259	
6	16	0	505	-496	4	2	1	225	-224	0	6	2	561	570	6	23	2	209	-16	3	3	969	-981	
6	24	0	264	161	4	3	1	444	-436	0	10	2	506	-511	7	0	2	426	-429	3	4	3	342	344
8	0	0	338	-289	4	4	1	213	-218	0	12	2	418	-438	7	1	2	222	-219	3	5	3	623	-630
8	1	0	248	248	4	5	1	215	-211	0	14	2	253	-250	7	2	2	213	215	3	6	3	213	-222
8	2	0	375	365	4	6	1	270	261	0	22	2	255	216	7	4	2	195	172	3	7	3	543	519
8	3	0	222	-209	4	7	1	888	898	1	0	2	2117	-2061	7	5	2	130	118	3	8	3	108	104
8	5	0	114	59	4	9	1	282	291	1	1	2	514	-500	7	6	2	263	288	3	9	3	393	382
8	6	0	229	251	4	12	1	143	-191	1	2	2	1502	1478	7	8	2	275	299	3	11	3	592	585
8	7	0	104	104	4	15	1	207	167	1	3	2	629	620	7	9	2	599	623	3	12	3	213	-236
8	8	0	140	104	4	16	1	148	-76	1	4	2	283	-276	7	10	2	142	-120	3	13	3		

Table 1. Continued.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
6	2	3	317	327	2	2	4	390	-384	10	0	4	318	-314	7	3	5	402	-428
6	3	3	469	-483	2	2	4	551	-554	10	4	4	387	-390	7	5	5	157	-185
6	4	3	418	412	2	2	3	844	-858	10	6	4	166	-83	7	8	5	177	-158
6	5	3	399	423	2	5	4	826	-828	10	12	4	363	351	7	9	5	203	-304
6	7	3	199	-183	2	7	4	845	-851	11	0	4	355	349	7	10	5	215	-178
6	8	3	248	-265	2	10	4	497	501	11	1	4	163	162	7	11	5	237	-242
6	15	3	224	202	2	11	4	291	-281	11	3	4	208	195	7	13	5	176	-121
7	1	3	586	581	2	13	4	303	267	12	0	4	363	382	8	8	5	322	279
7	2	3	263	-211	3	0	4	358	365	12	3	4	344	290	9	1	5	170	-168
7	3	3	756	764	3	12	4	320	-247	0	2	5	245	254	9	2	5	201	-160
7	4	3	307	-284	3	4	4	192	199	12	7	4	205	240	9	6	5	307	-299
7	5	3	177	182	3	5	4	271	-264	12	13	4	216	37	10	2	5	176	-153
7	7	3	203	212	3	8	4	135	-105	13	2	4	190	-182	10	4	5	180	-156
7	9	3	370	-368	3	11	4	151	125	14	0	4	225	201	11	1	5	326	-316
7	10	3	298	290	3	12	4	225	247	0	2	5	245	254	11	4	5	192	151
7	11	3	360	-361	3	13	4	200	-165	0	4	5	269	-277	11	6	5	202	253
7	13	3	331	-324	3	14	4	264	-278	0	8	5	201	191	0	0	6	798	790
7	15	3	389	-385	4	0	4	570	-575	0	14	5	173	-134	0	2	6	625	632
8	1	3	113	-45	4	1	4	435	435	1	1	5	269	270	0	4	7	727	725
8	2	3	232	243	4	3	4	122	-119	1	2	5	284	-286	0	8	6	397	-404
8	3	3	133	153	4	4	4	306	-302	1	4	5	645	651	0	10	6	404	-423
8	6	3	268	264	4	6	4	213	-224	1	6	5	444	-446	0	12	6	367	-344
8	7	3	292	284	4	7	4	494	507	1	8	5	537	-547	0	14	6	174	-179
8	8	3	186	-182	4	8	4	474	484	1	10	5	239	-272	1	0	6	490	473
8	9	3	134	69	4	10	4	247	227	1	11	5	146	-168	1	1	6	171	-177
8	10	3	164	-145	4	11	4	601	-616	1	16	5	295	-284	1	3	6	381	-379
8	11	3	216	-215	4	12	4	457	474	2	1	5	334	334	1	4	6	213	-217
9	1	3	251	-275	4	13	4	163	-179	2	2	5	428	-437	1	8	6	215	-225
9	2	3	486	-488	4	15	4	158	-128	2	4	5	243	224	1	9	6	213	224
9	3	3	374	-380	4	19	4	308	-279	2	5	5	248	-221	1	10	6	161	92
9	4	3	292	-295	5	1	4	287	-276	1	11	6	159	151	1	11	6	159	151
9	6	3	587	588	5	2	4	155	144	2	7	5	299	305	2	2	6	238	-227
9	9	3	191	191	5	5	4	162	-155	2	8	5	206	185	2	5	6	168	-205
9	11	3	163	193	5	6	4	254	-246	2	10	5	143	129	2	8	6	153	-175
9	14	3	299	284	5	7	4	202	209	2	12	5	167	-171	2	9	6	166	-102
9	18	3	224	195	5	10	4	287	288	2	14	5	194	209	2	12	6	203	180
10	2	3	148	-169	5	11	4	240	252	3	1	4	258	-246	2	15	6	213	211
10	3	3	152	-136	5	18	4	221	-71	3	2	5	281	-284	2	16	6	211	190
10	4	3	190	204	6	0	4	648	643	3	3	5	137	-99	3	0	6	219	207
10	5	3	279	260	6	2	4	495	503	3	4	5	132	-136	3	2	6	347	342
10	11	3	165	108	6	3	4	198	-190	3	5	5	252	-245	3	3	6	224	-228
11	1	3	181	-144	6	4	4	180	-164	3	6	5	295	-284	3	4	6	152	-122
11	3	3	193	-172	6	5	4	148	153	3	7	5	263	258	3	5	6	227	-229
11	6	3	243	217	6	6	4	275	-275	3	8	5	200	-200	3	6	6	205	-197
11	9	3	175	130	6	7	4	153	130	3	9	5	138	162	3	8	6	213	-179
11	13	3	241	243	6	9	4	596	590	3	11	5	167	200	3	11	6	285	303
13	1	3	403	376	6	10	4	221	-203	3	13	5	216	222	3	12	6	191	166
13	3	3	377	369	6	14	4	193	-213	3	14	5	281	281	4	0	6	756	-762
13	4	3	208	179	6	17	4	217	-226	4	2	5	194	-188	4	0	6	407	-398
13	9	3	288	-281	7	4	4	151	-155	4	3	5	191	-171	4	3	6	407	418
13	12	3	205	-88	7	5	4	124	-142	4	4	6	276	-282	4	4	6	196	-209
0	0	4	536	-540	7	10	4	405	-424	4	5	5	405	405	4	5	6	252	265
0	2	4	1168	1192	7	10	4	182	163	4	7	5	219	-220	4	11	6	179	-143
0	4	4	422	-418	7	12	4	161	183	4	11	5	193	-166	4	13	6	226	-220
0	8	4	184	201	8	0	4	698	694	4	13	5	174	65	4	14	6	304	299
0	10	4	378	-385	8	3	4	477	-465	5	1	5	129	131	4	18	6	227	34
0	14	4	507	-495	8	5	4	611	-640	5	2	5	219	216	5	0	6	258	292
0	15	4	302	-300	8	6	4	313	-311	5	3	5	181	-167	5	4	6	209	-198
0	22	4	284	244	8	7	4	206	-174	5	4	5	596	576	5	6	6	278	-268
1	0	4	256	-254	8	8	4	195	-204	5	5	5	209	203	5	7	6	168	-91
1	1	4	138	-126	8	9	4	472	-496	5	6	5	614	612	5	10	6	170	116
1	3	4	489	-490	9	0	4	247	263	5	7	5	241	-261	5	11	6	226	-190
1	4	4	291	285	9	1	4	141	128	5	8	5	371	352	6	0	6	324	310
1	6	4	245	249	9	2	4	345	329	6	3	5	203	210	6	1	6	187	213
1	6	4	297	-304	9	5	4	142	-81	6	5	5	229	-190	6	2	6	241	242
1	7	4	239	231	9	6	4	183	-188	6	7	5	270	268	6	3	6	179	193
1	15	4	203	-168	9	7	4	259	-283	6	9	5	221	-216	6	4	6	225	230
1	22	4	208	181	9	8	4	197	-223	6	14	5	173	-112	6	5	6	232	203
2	0	4	141	156	9	10	4	183	-81	7	1	5	238	238	6	6	6	285	298

DISCUSSION

The nitro groups in the *p*-chlorophenyldinitromethanide anion are roughly coplanar. The phenyl group is twisted 71° from a planar conformation and plays no important part in the charge delocalization. The formal charge on the central carbon atom is therefore delocalized into the nitro groups; the conclusions of Kamlet and Glover<sup>2</sup> and Sitzman *et al.*<sup>3</sup> are thus verified. The conformation of the anion in the solid state is different from the one proposed by Torrsell *et al.*<sup>4</sup> for the divalent radical anions in solution.

Somewhat surprisingly the anion is not propeller shaped. The O21-N2-O22 group with a twist of 7° from a planar conformation has opposite pitch to that of the phenyl and the other nitro group. The twist angle for O11-

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
K <sup>+</sup>	14842	4226	-526	359	330	1249	-12	122	145
	8	6	18	8	4	27	13	36	24
Cl	29681	20220	12874	831	342	2507	643	536	325
	12	8	22	14	6	45	16	46	31
O11	-4456	42895	34557	536	338	843	78	-319	88
	26	17	48	33	16	84	35	92	67
O12	-16545	47344	17499	391	314	1522	299	-117	-125
	27	18	47	30	15	106	35	90	64
O21	-13598	46381	-16704	605	251	1720	345	-408	193
	29	18	47	36	15	110	39	107	65
O22	31	40543	-24968	613	362	1147	197	169	-31
	29	20	51	32	16	82	37	100	68
N1	-8293	43913	19041	377	212	1175	29	-34	72
	36	22	64	42	19	126	43	127	84
N2	-5839	42823	-12971	459	186	1217	-42	146	-35
	38	23	65	43	18	132	43	134	86
C0	-2983	41157	4779	409	175	756	7	-131	74
	40	26	73	46	20	130	47	129	85
C1	5375	36324	8169	440	138	943	99	-287	164
	41	24	64	49	19	137	52	131	82
C2	2624	30136	14243	453	217	1454	154	60	277
	36	27	71	47	20	142	56	144	107
C3	10049	25137	16331	660	201	1415	-83	-45	289
	42	29	66	47	19	143	64	173	107
C4	20404	26579	11992	575	216	1321	280	-148	198
	41	26	70	51	23	154	57	165	104
C5	23508	32773	6566	420	199	1567	150	7	-98
	37	28	66	48	19	156	58	135	99
C6	15977	37697	4584	385	172	1566	30	75	-126
	39	24	64	47	18	158	54	143	84

N1–O12 is 10°. Although one would expect a propeller to be the preferred conformation for a free anion, a twist similar to that found for the present compound has also been observed for the anion of rubidium dinitromethanide.<sup>9</sup> The anion of potassium 4,4-dinitro-2-butenamide<sup>10</sup> is essentially planar.

In the crystal structure of potassium phenyldinitromethanide<sup>11</sup> recently published a propeller shaped anion is found. The nitro groups are twisted 10° and the phenyl group 62° from the planar conformation. The central carbon atom is 0.06 Å out of the plane through N1, N2, and C1. Bond lengths and bond angle values are very similar to those found in this work.

For the *p*-chlorophenyldinitromethanide anion the central carbon atom and its nearest neighbours are found to be coplanar within experimental errors. The CO–N1–O12 and CO–N2–O21 angles of 124.1° and 123.1° manifest the oxygen oxygen repulsion, O12 and O21 being 2.57 Å apart. An increase of the N1–CO–N2 angle may be hindered by repulsions between oxygen atoms and carbon atoms of the phenyl group (O11···C2 = 3.12 Å and O22···C6 = 3.04 Å) as well as by packing effects. The N–O and C–N distances with mean values of 1.256 Å and 1.389 Å are normal.<sup>1</sup>

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

Atom	$(\overline{u^2})^{\frac{1}{2}}$	$B$	$e_x$	$e_y$	$e_z$
K <sup>+</sup>	.264	5.49	0	49	21
	.188	2.79	34	-7	120
	.166	2.19	71	4	-58
Cl	.343	9.30	51	33	47
	.252	5.00	18	13	-127
	.166	2.17	-57	34	2
O11	.267	5.62	13	49	6
	.214	3.60	-73	7	46
	.143	1.62	26	-5	127
O12	.274	5.94	33	44	-22
	.204	3.28	3	8	133
	.151	1.81	72	-20	4
O21	.271	5.78	55	35	-8
	.231	4.23	-22	17	122
	.150	1.77	53	-30	58
O22	.284	6.36	31	46	1
	.214	3.61	70	-18	39
	.175	2.42	-21	5	129
N1	.212	3.54	9	48	29
	.181	2.58	37	7	-118
	.173	2.35	69	-10	58
N2	.205	3.33	51	-33	51
	.190	2.85	42	37	54
	.178	2.50	43	3	-113
C0	.192	2.91	-2	49	24
	.184	2.68	77	3	-30
	.141	1.57	18	-8	129
C1	.201	3.19	71	17	-38
	.184	2.67	-5	36	91
	.129	1.30	35	-29	92
C2	.240	4.54	32	38	68
	.193	2.94	53	7	-99
	.166	2.19	49	-31	61
C3	.240	4.56	-62	25	48
	.219	3.79	48	26	80
	.171	2.31	9	34	-97
C4	.254	5.08	56	35	14
	.203	3.25	-33	15	116
	.152	1.82	45	-32	68
C5	.223	3.92	37	37	-61
	.206	3.35	29	15	119
	.164	2.13	-63	29	19
C6	.214	3.62	4	-21	123
	.187	2.77	44	38	43
	.172	2.34	-66	24	37

Table 4. Bond distances and angles of the anion, short *intra*-molecular contacts and other contacts (equivalent position numbers in parentheses as defined in Table 6).

Bond distances (Å)		Bond angles (°)	
C0-N1	1.372	N1-C0-N2	119.8
C0-N2	1.406	C1-C0-N1	119.6
C0-C1	1.464	C1-C0-N2	120.5
N1-O11	1.266	C0-N1-O11	116.5
N1-O12	1.261	C0-N1-O12	124.1
N2-O21	1.250	O11-N1-O12	119.4
N2-O22	1.248	C0-N2-O21	123.2
C1-C2	1.377	C0-N2-O22	115.1
C2-C3	1.391	O21-N2-O22	121.6
C3-C4	1.382	C1-C2-C3	121.9
C4-C5	1.375	C2-C3-C4	117.5
C5-C6	1.388	C3-C4-C5	122.2
C6-C1	1.397	C4-C5-C6	119.3
C4-C1	1.745	C5-C6-C1	119.9
<i>Intra</i> -molecular contacts (Å)		C6-C1-C2	119.2
O12...O21	2.57	C0-C1-C2	118.8
O11...C1	2.67	C0-C1-C6	122.0
O22...C1	2.69	Cl-C4-C3	118.3
O11...C2	3.12	Cl-C4-C5	119.5
O22...C6	3.04		
Other contacts (Å)			
Cl...N2(3)	3.21		
Cl...C0(3)	3.44		
Cl...C5(3)	3.39		

Table 5. Deviations of atoms from least squares planes. 1 is through the central carbon atom and its neighbours. 2 is through the atoms of the phenyl group. Deviations of atoms not defining the planes in parentheses.

Atom	1	Atom	2
C0	0.012	C1	-0.017
C1	-0.004	C2	0.008
N1	-0.003	C3	0.010
N2	-0.003	C4	-0.019
O11	( 0.189)	C5	0.009
O12	(-0.188)	C6	0.008
O21	(-0.130)	Cl	(-0.144)
O22	( 0.134)	C0	(-0.137)
C2	(-1.161)		
C6	( 1.096)		

Table 6. Coordination distances of the potassium ion.

Atom	Equiv. pos.	No.	(Å)
O11	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$	1	2.90
O11	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	2	2.75
O12		1	2.83
O12	$\frac{1}{2}+x, \frac{1}{2}-y, -z$	3	2.69
O21		3	3.02
O21	$-x, -\frac{1}{2}+y, -\frac{1}{2}-z$	4	2.91
O22	$x, \frac{1}{2}-y, \frac{1}{2}+z$	5	2.87

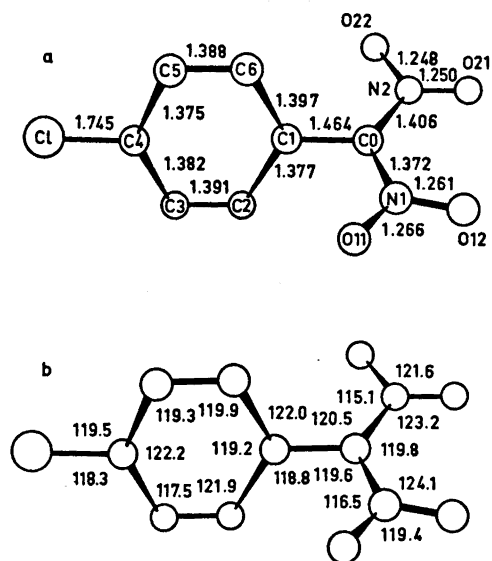


Fig. 1. Bond distances (a) and angles (b) of the anion.

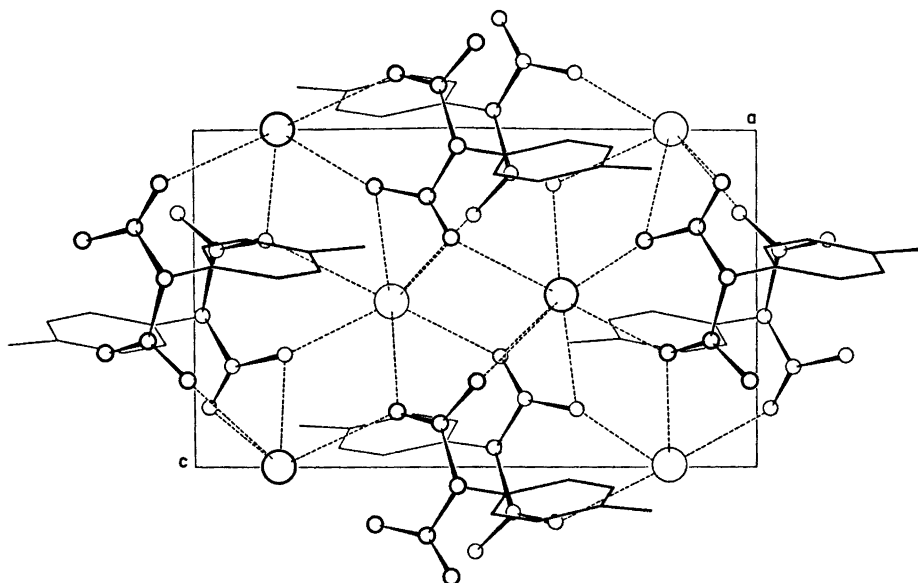


Fig. 2. A schematic drawing of the structure viewed along the  $b$  axis (cation contacts dotted).



Whereas the large twist of the phenyl group is caused mainly by *intra*-molecular repulsions, the non-planarity of the phenyl group and the atoms bonded to it (plane 2 of Table 5) is probably due to packing effects. Although the chlorine atom is situated 0.14 Å below the plane through the phenyl ring it has short contacts to the anion above, related to the first by a glide plane along *c*. The C0–C1 and Cl–C4 bonds form angles of 4.7° and 4.1° with plane 2. The phenyl ring itself is not significantly non-planar. However, the deviations of all atoms from plane 2 indicate that it may be slightly boat-shaped. The C0–C1 bond length of 1.464 Å is within the limits of error not different from the normal single bond value between *sp*<sup>2</sup> carbon atoms. The Cl–C4 bond length (1.745 Å) is close to the average value for an "isolated" carbon chlorine bond in the case of aromatic compounds, reported by Rudman to be 1.737 Å.<sup>12</sup>

The coordination about the potassium ion is rather irregular as may be seen from Fig. 2. All but one oxygen atom (O22) are coordinated to two potassium ions, and a two-dimensional network (along *a* and *c*) determined by the ionic forces is formed. van der Waals forces between phenyl groups from different layers complete the three-dimensional arrangement. It may also be noted that the chlorine atom has the largest anisotropic motion (Table 2). The coordination about the potassium ion is very similar to that found for potassium phenyldinitromethanide.<sup>11</sup> The crystal packing of the two compounds differs mainly in the stacking of the ionic layers.

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#### REFERENCES

1. Klewe, B. *Acta Chem. Scand.* **26** (1972) 1049.
2. Kamlet, M. J. and Glover, D. J. *J. Org. Chem.* **27** (1962) 537.
3. Sitzmann, M. E., Adolph, H. G. and Kamlet, M. J. *J. Am. Chem. Soc.* **90** (1968) 2815.
4. Torssell, K., Lagercrantz, C. and Wold, S. *Arkiv Kemi* **29** (1968) 219.
5. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømning, C. *Acta Chem. Scand.* **24** (1970) 2232.
6. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
7. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3178.
8. Schomaker, V. and Trueblood, K. N. *Acta Cryst.* **B 24** (1968) 63.
9. Grigor'eva, N. V., Margolis, N. V., Shokhor, I. N., Tselinskii, I. V. and Mel'nikov, V. V. *J. Struct. Chem. (USSR) (Eng. Transl.)* **9** (1968) 475.
10. Holden, J. R. and Dickinson, C. *J. Am. Chem. Soc.* **90** (1968) 1975.
11. Grigor'eva, N. V., Margolis, N. V., Tselinskii, I. V. and Shokhor, I. N. *Zh. Strukt. Khim.* **11** (1970) 165.
12. Rudman, R. *Acta Cryst.* **B 27** (1971) 262.

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