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The Crystal Structure of Dipotassium Nitroacetate

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Dipotassium nitroacetate is orthorhombic, $Pbm\text{–}C_{2v}^{2}$ with two molecules of $K_2C_2HNO_4$ in a unit cell of dimensions $[a] = 10{\cdot}28$, $[b] = 7{\cdot}49$, $[c] = 3{\cdot}54$ Å. The nitroacetate ions lie on a mirror plane at $z = 0$, whilst the four potassium ions lie on a mirror plane at $z = \frac{1}{2}$ and are in eightfold coordination with oxygens of the anion.

Introduction

Dipotassium nitroacetate was first prepared from nitromethane by Steinkopf (1909). The free acid has long been recognized as dibasic with $K_1 = 2{\cdot}08 \times 10^{-2}$ (Pederson, 1934) and K_2 about 10^{-9} (Heuberger, 1928). The considerable effect which a nitro group in the α position has upon the behaviour of the carboxyl group (for acetic acid $K = 1{\cdot}8 \times 10^{-5}$) suggests that by mutual interaction the dimensions and properties of the nitro group might be modified. For this reason it was thought that the crystal structure of dipotassium nitroacetate should prove interesting, especially when it was found that the anion and cations lay in special positions such that [c] parameters were determined by symmetry.

The structure of the free acid is also being investigated in order to compare the dimensions of a nitro group in which the *aci*-form probably predominates, with the NO_2^- derived from the *aci*-form by removal of the hydrogen ion.

Experimental

Dipotassium nitroacetate is prepared in the following manner:

Nitromethane (50 g.) is added to a 1:1 potassium-hydroxide solution (250 ml.). A temperature of about 45–50° C. must be maintained till addition is complete, but may then be permitted to rise to about 55° C. A spontaneous fall in temperature indicates the end of the first reaction.

The mixture is heated to boiling (10 min.) with the evolution of ammonia. Dipotassium nitroacetate then separates out and is recrystallized from hot 1:1 potassium-hydroxide solution.

The crystals are well developed orthorhombic needles exhibiting {010} and {110}; there is good cleavage perpendicular to the direction of elongation. The optical sign is negative and the refractive indices are

$$\alpha = 1{\cdot}423 \text{ (parallel to } [c]); \ \beta = 1{\cdot}659 \text{ (parallel to } [a]); \ \gamma > 1{\cdot}659 \text{ (parallel to } [b]).$$

Unit-cell dimensions were obtained from rotating-crystal photographs and reflexions were indexed on equi-inclination Weissenberg photographs; the cell dimensions are

$$[a] = 10{\cdot}28,\ [b] = 7{\cdot}49,\ [c] = 3{\cdot}54 \text{ Å}.$$

The density measured by flotation, is between 2·172 and 2·208 g.cm.$^{-3}$; the value calculated for 2 molecules of $K_2C_2HNO_4$ per cell is 2·208 g.cm.$^{-3}$. Absent spectra are $\{0kl\}$ when $k \neq 2n$; the space group is either *Pbmm* or *Pbm*.

Intensity data for all the reflexions $\{hkl\}$ obtainable with Cu $K\alpha$ radiation were recorded on equi-inclination Weissenberg photographs. Because of the very deliquescent nature of this substance, the single crystals were enclosed in perspex capsules containing a small amount of anhydrone as desiccant (Llewellyn, 1951). No correction for absorption in the crystal was made, but corrections were made for varying path lengths of the diffracted beam through the walls of the capsule. The intensities were estimated visually by comparison with a standard scale and the resulting table of relative structure amplitudes was made approximately absolute by comparing the observed and calculated values for the orders of $00l$. More accurate correlation was obtained later by direct comparison of the observed values and those calculated from the structure using the most suitable scattering curves for C, N, O and K^+.

The three-dimensional Fourier sections at $z = 0$, and $z = \frac{1}{2}$, and the three-dimensional difference Fouriers were computed using Robertson's strips. In the difference Fouriers, three-figure accuracy at intervals of 3° was achieved.

Structure determination

The morphology of a large number of crystals gives no indication of a mirror plane perpendicular to [b]. The absence of a centre of symmetry is also indicated by the pronounced pyro-electric properties on cooling with liquid air. A mirror plane and a glide plane may be combined in two ways in the orthorhombic system;

the mirror may be either perpendicular to or parallel to the direction of the glide. The morphological data quoted above indicates the latter possibility, and this was later confirmed by a Patterson projection on to 001 which exhibited no peaks with coordinate $x = 0$ other than the peak at the origin. The space group is therefore C_{2v}^2, which may be written $Pb2_1m$ in order to distinguish it from C_{2v}^4.

The atoms of the anion must lie in one of the two sets of special twofold positions of C_{2v}^2:

$$(a)\quad x, y, 0;\ \bar{x}, \tfrac{1}{2}+y, 0;$$
$$(b)\quad x, y, \tfrac{1}{2};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}.$$

The distinction between these is arbitrary and consequently the planar anion was placed on the mirror plane at $z = 0$. The four potassium ions may be in general positions, or they may exist as two crystallographically dissimilar pairs disposed on either or both of the mirror planes. The shortness of the c axis (3·54 Å) and the large ionic radius of K^+ (1·33 Å) precludes the possibility that these ions are in general positions. Of the three possible arrangements of two pairs of potassium ions in the two sets of special positions the correct choice can readily be made by comparing the observed and calculated values for the structure amplitudes of the orders $00l$. All the potassium ions lie on the mirror plane for which $z = \frac{1}{2}$.

The x and y coordinates of the anion were readily obtained by means of paper models constructed with conventional bond distances and inter-bond angles of 120°, while the x and y coordinates of the potassium ions were determined by a Patterson projection on to 001 in conjunction with the packing model. Only one arrangement proved suitable and this agreed satisfactorily with the observed optical properties. These coordinates were then refined by ten successive two-dimensional Fourier projections on to 001.

The scattering curve of the potassium ion does not remain strictly proportional to that of carbon for all ϱ values. The ratio of f_{K^+}/f_C was obtained from data calculated by Viervoll & Ögrim (1949) and the contributions of the potassium ions were multiplied by a correction factor q, so that the molecular structure factor could be calculated in the following manner:

$$F_c = 2(\sum_{1}^{R} NPq)f_c/6$$

where N = atomic number; P = structure amplitude function $\sqrt{(A^2+B^2)}$; q is unity for C, N and O, and has the following values for K^+:

ϱ	q
0 –0·25	1·00
0·26–0·59	1·25
0·60–0·80	1·44
0·81–1·60	1·52
1·61–1·80	1·48

The large peaks of the potassium ions produced considerable distortion in the peaks corresponding to the atoms of the anion, so that accurate coordinates could not be obtained by this method. In fact, at this stage it was not possible to distinguish between the carboxyl and the nitro group. Further refinement by means of three-dimensional Fourier sections at $z = 0$ and $z = \frac{1}{2}$ did little to resolve this difficulty. The two bonds from the central carbon atom, one of which is C–N and the other C–C were 1·33 Å and 1·40 Å, and the two end groupings ($-NO_2^-$ and $-CO_2^-$) gave bond distances of 1·30 Å, 1·24 Å, and 1·33 Å, 1·15 Å, neither of which pair could be unequivocally associated with a nitro or carboxyl group.

In order to accelerate the refinement of the coordinates, three-dimensional difference sections at $z = 0$ and $z = \frac{1}{2}$ were evaluated (Booth, 1948; Cochran, 1951). In this method, the true electron density at the atomic centres is required, and hence the absolute scale of F must be known. Comparison of observed and calculated F's gave a scaling factor and this set of absolute F's was then compared with a set obtained by another method.

Harker (1948) has shown that if F'_{hkl} represents a structure factor on an arbitrary scale and F_{hkl} the same structure factor on an absolute scale, a conversion factor K can be defined by the relation

$$F'_{hkl} = KF_{hkl}\,.$$

Then K can be computed from the relation

$$K^2 = \left(\overline{|F'_{hkl}|^2} \Big/ \sum_{j=1}^{n} f_j^2\right),$$

where the square of the numerical value of each structure factor on the relative scale is divided by the sum of the squares of the atomic scattering factors in the unit cell and an average is taken over all reflexions used.

These two methods gave two sets of F absolute which showed greater discrepancies than would be expected from the application of this equation to a structure containing potassium ions. In both of these methods F calculated was evaluated using for the potassium ion a scattering curve which was deduced from scattering curves for chlorine and potassium given by Viervoll & Ögrim (1949). The discrepancies between the two sets of F absolute could therefore be due to the use of the wrong scattering curve, but at the time it was thought that the structure was not accurate enough to calculate a scattering curve from it and so D. 1, the first three-dimensional difference Fourier, was completed. Δ was calculated for each atom and the shifts were made in the direction of steepest ascents. The maximum value of Δ was 0·15 Å.

A second difference Fourier was calculated and by this time the bond lengths had changed considerably. The reliability factor R, defined by the equation

$$R = \Sigma(|F_o|-|F_c|) \div \Sigma F_o\,,$$

was calculated from the coordinates from D. 2 and this remained constant at 0·244. A comparison of F_o and F_c showed that planes of low ϱ values were calculating too small and planes of high ϱ values were calculating too big. The use of a carbon-like scattering curve in place of that for a potassium ion did not improve the agreement, as was shown by the value of 0·242 for R. Complete refinement could not be obtained, then, until a more suitable scattering curve was calculated. The possibility of constructing two curves, one for the potassium ions and one for the anion, was first investigated. However, there were not sufficient planes in which the potassium contribution was small to enable a scattering curve for carbon to be obtained and then utilized in the calculation of a scattering curve for the potassium ions, so a compromise had to be made. Comparison of the scattering curves for pentaerythritol tetranitrate (Llewellyn & Booth, 1947), pentaerythritol (Cox, Llewellyn & Goodwin, 1937) and carbon (Viervoll & Ögrim, 1949) showed they were similar for ϱ values less than 0·80 but the rest of the curve was peculiar to the structure. The new scattering curve was constructed in the following way. For ϱ values up to 0·80 the scattering curve f_C was taken from the values of Viervoll & Ögrim and then used to evaluate F_c for the thirty planes within these limits. It was found that for these planes $\Sigma F_c / \Sigma F_o = 0{\cdot}688$.

This factor of 0·688 was used to convert F_o to F absolute per cell and the latter portion of the curve was constructed from the equation

$$f = F_{hkl,\,\text{abs.}} / F'_{hkl,\,\text{calc.}} \,,$$

where $F'_{hkl,\,\text{calc.}} = \varphi(hkl)\ (x, y, z)$ for the planes with ϱ greater than 0·80.

The variation in the mean scattering curve for carbon in dipotassium nitroacetate with $\sin\theta$ is given below.

$\sin\theta$	0	0·1	0·2	0·3	0·4	0·5
f_C	6·0	5·34	4·14	3·06	2·43	2·04

$\sin\theta$	0·6	0·7	0·8	0·9	1·0
f_C	1·77	1·47	1·26	1·05	0·81

On recalculation, the reliability factor R was reduced to 0·163. D. 3 was calculated and the largest shift was 0·07 Å. The bond lengths were still showing appreciable changes but this was to be expected owing to the erroneous differences used in previous Fouriers. D. 4 reduced the value of R to 0·150 and the gradient round many of the atoms had been completely removed.

It was now thought that reliability factors could be used to distinguish between the carboxyl and nitro groups. F_c was evaluated first with the N atom as nitrogen and secondly with C_1 as nitrogen, and two reliability factors were calculated. The value of 0·150 for the former compared with 0·151 for the latter was slightly in favour of N as nitrogen.

Reliability factors for the different zones of planes were calculated and showed that R for the $\{h0l\}$ planes was much higher than any other value of R:

$$R_{h0l} = 0{\cdot}238,\ R_{0kl} = 0{\cdot}080,\ R_{hk0} = 0{\cdot}146\,.$$

As the differences between F_o and F_c were much smaller, the first decimal place was included in the summation, thus eliminating rounding-off errors. The new coordinates obtained from the correction Δ gave the following values of R for D. 5:

$$R_{hkl}\ (\text{all planes}) = 0{\cdot}146,\ R_{h0l} = 0{\cdot}244,\ R_{0kl} = 0{\cdot}076,\ R_{hk0} = 0{\cdot}134\,.$$

Attempts were now made to improve the $\{h0l\}$ planes, which were not refining and which were considerably in error compared with other planes. $\{h0l\}$ planes could be calculating incorrectly owing to wrong x or z coordinates. The possibility of the z coordinates being in error was first considered; $\{0kl\}$ with k odd is the only space-group halving. The crystal could be monoclinic with $\beta = 90°$, giving the space group Pb with $[a]$ the symmetry axis. The absence of the mirror plane perpendicular to $[c]$ would then allow for small shifts in the z coordinates, but no difference in the intensities of $0kl$ and $0k\bar{l}$ was observed, thus excluding this. The other possibility, that the x coordinates were in error, could be due to the anisotropic vibration of the heavy atoms. $\{h0l\}$ and $\{0kl\}$ projections were calculated and the $\{h0l\}$ projection showed that the electron density round K_1 was not circularly symmetrical. If this asymmetry was due to anisotropic vibration, the scattering curve could be represented by

$$f = f_o \exp\left[-\{\alpha + \beta \sin^2(\varphi - \psi)\} s^2\right]$$

(Cochran, 1951; Hughes, 1941), where α and β are constants, ψ is the angle between the direction of maximum vibration and $[c]$ and $(2s, \varphi)$ are the polar coordinates of a point in the plane $k = 0$ of the reciprocal lattice. The planes were grouped into five sets, each centred around one of $\varphi = 10°, 30°, \ldots, 90°$, but no constant values of α and β were obtained. It was assumed that the discrepancies in the $\{h0l\}$ planes were too great to permit any calculation of scattering curves which were corrected for anisotropic vibration. These $\{h0l\}$ planes are the only centrosymmetric planes and as other planes could not be used to determine this anisotropic-vibration-correction for a single potassium ion, other means of attack were tried to improve the agreement in the $\{h0l\}$ planes.

Two $\{h0l\}$ difference Fourier projections were calculated and from these the x coordinates of K_1 and K_2 were obtained. The value of R_{h0l} was 0·212, showing slight improvement. These coordinates were used in calculating structure amplitudes for the $\{hkl\}$ planes, the other coordinates being as in D. 5, but the overall value of R was increased. The agreement was finally improved in the following way. Planes of too small measurable intensity had been put into Fouriers as zero; now one-half the smallest measurable value was used and R was recalculated:

$$R_{hkl} = 0{\cdot}128,\ R_{h0l} = 0{\cdot}168,\ R_{0kl} = 0{\cdot}079,\ R_{hk0} = 0{\cdot}128.$$

A certain peak in D. 5 could be reasonably ascribed to a hydrogen atom, and from the peak the coordinates of this atom were obtained. The value of Δ was then calculated from D. 5 and no change was observed in the coordinates of the majority of the atoms, the others exhibiting shifts of 0·001 or 0·002. These coordinates were taken as final.

The final value of R was evaluated in the following way. Dipotassium nitroacetate is an ionic salt and throughout this work the potassiums have been treated as potassium ions, leaving four electrons per cell over. These four electrons were then evenly distributed among the oxygen atoms, and the N atom was weighted as nitrogen, whence

$$R_{hkl} = 0{\cdot}126,\ R_{h0l} = 0{\cdot}167,\ R_{0kl} = 0{\cdot}077,\ R_{hk0} = 0{\cdot}128.$$

The final coordinates were used to calculate an electron-density map; the $z = 0$ and $z = \frac{1}{2}$ sections are combined in Fig. 1. The atoms are completely resolved, the contours round each being circularly symmetric. Sometimes, as in decaborane (Kasper, Lucht & Harker, 1950), the hydrogen atoms appear in electron-density maps, but no indication of the presence of the hydrogen can be seen in this map. This is not unexpected as it forms such a very small portion of the diffracting matter in the cell. The greater volume of the N atom peak compared with that of C_1 was the final proof that the nitro group and the carboxyl group have been correctly identified.

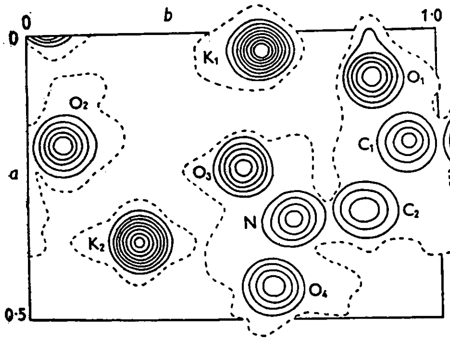


Fig. 1. Final electron-density map obtained by computing sections at $z = 0$ and $z = \frac{1}{2}$. Contours at intervals of 3 e.Å^{-3} for carbon, nitrogen and oxygen; and 6 e.Å^{-3} for the potassium ions. Zero contour broken.

Observed and calculated structure factors are given in Table 1.

Discussion of structure

The fractional coordinates obtained from D. 5 are:

	x/a	y/b	z/c
K_1	0·033	0·579	0·500
K_2	0·369	0·275	0·500
N	0·333	0·645	0
C_1	0·200	0·921	0
C_2	0·316	0·829	0
O_1	0·084	0·842	0
O_2	0·201	0·090	0
O_3	0·242	0·528	0
O_4	0·451	0·598	0
H	0·386	0·903	0

Bond lengths and bond angles calculated from these coordinates are shown in Fig. 2, which is a diagram of the anion.

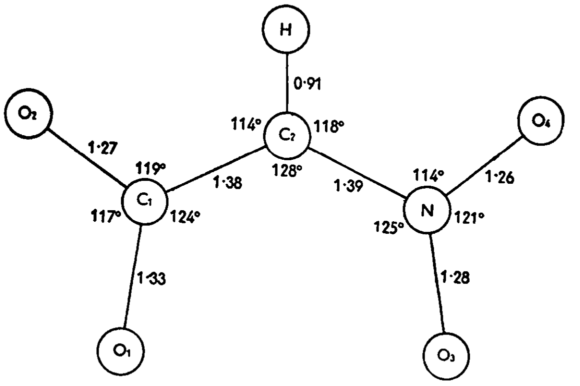


Fig. 2. Diagram of the anion, showing bond lengths and bond angles.

The standard deviation of bond length was calculated from Booth's equation (1947)

$$\sigma(x_r) = (2/N_r)(\pi/\lambda p)^2(\pi/V)^{\frac{1}{2}}\sigma(F_o)\ ,$$

where

$\sigma(x_r)$ is the standard deviation of the x coordinate of the rth atom,
N_r is its atomic number,
λ = 1·539 for Cu $K\alpha$,
p = 4·9 for a carbon atom,
$\sigma(F_o) = \{\overline{(\Delta F_o)^2}\}^{\frac{1}{2}}$ and
V is the volume of the unit cell.

An upper limit to the value of $\sigma(F_o)$ is got by taking

$$\sigma(F_o) = 1{\cdot}25\overline{|F_o - F_c|}\ .$$

Hence, for a carbon atom, $\sigma(x_r)$ is not greater than 0·011 Å. Therefore the standard deviation in bond length does not exceed 0·02 Å. This gives a value not greater than 1° for the standard deviation in a bond angle.

The structure consists of alternate layers of anions and cations separated by a distance along the [c] of 1·77 Å. Since the anion is situated on a plane of symmetry all its atoms, including the hydrogen, are coplanar. In the formation of the anion from the acid, the *aci*-form of the latter must exist as an intermediate form, thus:

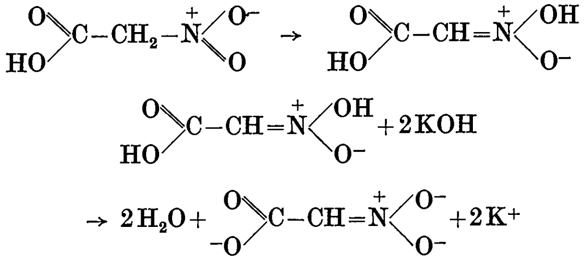
Table 1. *Observed and calculated structure factors and phase angles*

In the following table *n* indicates not observed on Weissenberg photographs and *h* indicates space-group halving

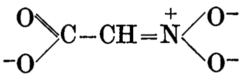
Plane	F_o	F_c	α (°)
100	*n*	9·0	0
200	< 1·4	2·7	0
300	33·8	39·8	0
400	< 2·0	1·1	180
500	23·7	22·8	0
600	9·2	8·7	0
700	25·5	27·7	180
800	5·6	1·6	180
900	< 3·4	4·0	0
10,0,0	9·0	11·0	180
11,0,0	3·1	1·2	0
12,0,0	9·7	14·9	180
010	*h*		
110	8·3	7·8	284
210	27·4	35·1	27
310	18·4	18·8	278
410	24·4	25·5	314
510	40·0	44·5	323
610	19·7	19·3	211
710	21·8	25·1	333
810	13·9	15·1	290
910	27·0	30·8	250
10,1,0	18·0	20·5	328
11,1,0	< 3·0	4·4	152
12,1,0	< 2·6	5·0	226
020	22·6	25·6	89
120	29·2	36·2	22
220	18·2	17·0	76
320	24·4	21·7	168
420	45·1	48·8	34
520	18·7	13·7	60
620	14·1	9·9	134
720	14·9	15·2	35
820	14·6	15·0	216
920	6·0	5·9	37
10,2,0	11·6	11·6	263
11,2,0	12·9	16·7	218
12,2,0	4·7	7·1	275
030	*h*		
130	30·2	30·0	355
230	28·6	26·6	232
330	31·5	31·2	14
430	17·8	17·3	342
530	22·7	19·1	300
630	25·4	27·5	12
730	12·1	11·3	17
830	6·0	5·7	357
930	21·6	27·2	17
10,3,0	3·2	3·8	285
11,3,0	4·6	5·4	18
12,3,0	7·1	10·4	12
040	48·4	48·9	100
140	20·6	21·3	144
240	19·5	20·0	127
340	21·3	23·3	72
440	15·2	15·4	160
540	9·3	11·2	53
640	6·5	3·0	172
740	10·8	10·6	227
840	17·9	22·9	6
940	6·6	7·9	198
10,4,0	9·3	9·4	242
11,4,0	4·1	6·1	5
12,4,0	5·3	9·0	261
050	*h*		
150	18·0	17·4	226
250	20·2	21·8	23
350	16·6	16·7	125
450	18·2	15·9	114
550	27·0	32·0	40
650	11·4	11·3	275
750	16·4	19·3	69
850	16·4	19·3	40
950	6·0	6·3	27
10,5,0	16·1	16·1	47
060	25·3	26·6	207
160	17·1	17·1	111
260	14·1	13·9	171
360	12·0	9·7	238
460	16·0	17·4	110
560	22·2	24·3	191
660	14·2	11·0	230
760	6·5	8·7	58
860	4·1	1·8	246
960	5·4	4·7	358
10,6,0	5·4	5·0	21
070	*h*		
170	14·1	12·5	23
270	8·9	6·3	242
370	21·6	22·8	102
470	14·9	14·8	79
570	8·5	8·1	149
670	13·0	13·3	66
770	8·4	8·5	167
870	10·2	9·6	129
970	11·0	13·3	97
080	8·3	7·0	201
180	20·0	19·4	232
280	15·8	15·8	251
380	< 2·8	5·4	108
480	14·1	13·6	239
580	4·5	3·8	111
680	< 2·2	2·6	98
780	7·8	7·5	264
090	*h*		
190	8·5	8·6	284
290	10·3	9·5	94
390	9·1	11·7	221
490	4·5	3·6	207
001	21·2	19·7	0
101	13·1	9·6	180
201	44·5	39·4	180
301	46·5	46·7	180
401	18·9	13·0	0
501	22·5	20·6	180
601	17·4	12·9	180
701	3·8	3·4	0
801	22·6	25·4	180
901	20·7	23·2	0
10,0,1	14·1	13·8	0
11,0,1	< 3·6	0·2	180
12,0,1	12·9	17·2	0
011	*h*		
111	43·1	36·7	19
211	48·2	41·8	146
311	25·3	22·4	42
411	19·5	16·4	66
511	23·3	24·9	165
611	28·6	28·3	84
711	21·4	20·2	122
811	23·9	23·5	149
911	4·3	3·1	350
10,1,1	14·4	13·7	164
11,1,1	14·3	16·3	107
12,1,1	4·4	6·9	77
021	21·8	22·1	343
121	49·5	49·6	232
221	38·3	31·8	224
321	18·1	13·4	252
421	19·5	19·6	213
521	20·6	15·9	13
621	4·5	3·1	194
721	16·4	16·2	187
821	17·5	17·6	19
921	11·6	9·1	187
10,2,1	6·2	4·1	220
11,2,1	13·1	16·6	34
12,2,1	3·0	5·1	167
031	*h*		
131	22·8	20·3	231
231	5·4	6·7	19
331	19·1	19·8	186
431	23·3	20·5	196
531	6·6	5·6	11
631	32·3	35·3	190
731	15·8	13·7	123
831	13·8	14·0	156
931	16·5	17·9	182
10,3,1	4·5	6·7	80
11,3,1	8·8	12·8	180
12,3,1	2·5	6·0	189
041	27·5	27·5	212
141	20·0	23·4	335
241	18·2	16·0	293
341	22·2	25·1	258
441	22·2	23·8	6
541	13·1	15·1	265
641	14·2	14·5	245
741	16·4	15·3	21
841	6·5	7·7	282
941	11·1	9·9	112
10,4,1	6·7	8·2	101
11,4,1	8·9	12·7	169
051	*h*		
151	< 3·8	3·1	[illegible]
251	28·1	29·3	241
351	14·9	13·2	119
451	17·3	16·6	182
551	21·1	20·8	239
651	12·7	13·5	291
751	16·3	18·4	211
851	12·8	11·2	233
951	5·8	7·7	8
10,5,1	12·1	15·0	230
061	25·2	25·5	17
161	13·6	13·0	335
261	14·9	13·1	337
361	28·1	30·9	12
461	9·8	9·9	250
561	8·0	4·8	121
661	3·9	5·3	310

Table 1 (*cont.*)

Plane	F_o	F_c	α (°)
761	8·3	10·2	240
861	14·7	15·4	62
961	4·3	6·9	220
071	*h*		
171	15·5	16·8	285
271	11·1	12·9	32
371	8·6	8·3	219
471	8·7	8·5	320
571	7·8	7·8	20
671	22·3	23·7	276
771	10·3	7·8	282
871	4·7	3·8	301
081	5·7	6·0	281
181	16·2	15·0	65
281	10·3	8·0	18
381	4·7	4·4	21
481	14·9	17·4	65
091	*h*		
191	7·2	8·2	24
291	10·3	9·2	292
002	66·1	68·8	0
102	11·6	5·6	0
202	< 6·4	4·2	0
302	25·0	27·3	0
402	< 6·4	1·0	180
502	19·7	17·4	0
602	11·8	6·7	0
702	22·5	21·8	180
802	< 8·4	1·3	180
902	< 8·0	3·2	0
012	*h*		
112	< 5·0	4·7	252
212	21·5	20·7	19
312	13·7	12·7	272
412	19·3	17·3	313
512	24·6	28·4	323
612	15·7	14·8	211
712	17·1	19·0	333
812	12·9	11·7	290
912	22·2	23·4	251
10,1,2	17·1	17·5	327
022	15·7	15·2	95
122	24·8	24·4	26
222	16·0	12·9	71
322	15·9	14·5	167
422	30·4	36·0	34
522	12·1	10·3	60
622	9·4	7·7	134
722	13·1	11·8	35
822	< 9·2	11·2	216
922	< 8·6	4·9	38
032	*h*		
132	22·6	20·6	355
232	19·9	19·6	232
332	19·6	23·6	14
432	13·8	13·2	342
532	16·9	15·0	300
632	22·7	21·5	12
732	13·3	8·9	17
832	< 7·8	4·6	357
932	17·4	22·0	17
042	30·5	36·4	100
142	18·0	16·0	144
242	14·7	15·0	127
342	16·9	17·8	72
442	10·9	12·0	160
052	*h*		
152	13·6	13·4	226
252	16·6	16·8	23
352	9·9	13·0	125
452	11·1	12·4	114
062	20·9	21·0	207
162	13·4	13·4	111
262	10·7	10·7	172
362	8·5	7·7	238
462	8·9	13·7	110
072	*h*		
172	12·5	10·0	22
272	< 7·0	5·0	243
372	18·1	18·4	102
472	13·2	12·2	78
082	7·5	5·8	201
182	16·6	15·5	232
282	12·1	12·9	251
382	< 4·0	4·2	108
482	9·1	10·7	239
003	9·6	8·1	0
103	7·2	4·9	180
203	22·4	20·4	180
303	23·7	25·0	180
403	< 7·8	7·7	0
503	14·9	12·2	180
603	11·6	8·0	180
703	< 7·8	2·0	0
803	19·0	16·6	180
903	18·3	15·3	0
013	*h*		
113	17·9	18·2	20
213	21·3	22·7	149
313	11·9	12·4	43
413	9·5	9·5	68
513	13·8	14·8	165
613	17·7	17·4	84
713	15·3	12·5	121
813	15·7	15·3	150
913	< 3·8	1·9	343
023	12·0	11·5	342
123	23·3	26·4	231
223	18·4	18·0	224
323	7·8	7·8	255
423	13·5	11·4	213
523	< 9·2	9·8	13
623	< 8·8	1·9	193
723	11·3	10·6	187
823	12·8	11·3	19
923	< 4·8	5·9	86
033	*h*		
133	11·8	12·4	229
233	< 8·0	3·9	19
333	13·2	11·9	186
433	11·6	12·6	197
533	< 7·6	3·5	8
633	19·4	22·5	190
733	9·4	8·9	122
833	8·5	9·3	156
933	8·9	11·1	182
043	19·8	16·8	213
143	13·1	14·2	205
243	12·9	10·0	293
343	13·6	15·6	258
443	13·0	14·8	7
053	*h*		
153	< 6·4	1·9	2
253	16·4	18·6	241
353	6·1	8·6	119
453	9·4	10·9	182
063	18·2	16·6	18
163	9·6	8·4	335
263	9·4	8·3	337
363	16·8	20·0	12
073	*h*		
173	9·6	10·5	285
273	4·5	8·2	31
004	29·6	33·1	0
104	< 6·0	2·8	0
204	< 6·6	1·9	0
304	11·1	13·6	0
404	< 5·6	0·4	180
504	10·8	8·9	0
604	5·6	3·2	0
014	*h*		
114	< 5·2	2·3	256
214	10·5	10·2	20
314	6·1	6·4	87
414	8·5	8·7	357
514	10·4	14·0	323
614	5·5	7·2	210
024	6·8	7·7	94
124	12·5	12·3	26
224	7·0	6·5	71
324	7·2	7·2	168
424	13·6	18·5	34
034	*h*		
134	9·6	10·4	355
234	7·7	9·9	232
334	11·6	12·1	14
434	5·4	6·7	341
044	13·6	18·5	100
144	9·2	8·1	144
244	7·5	7·4	127
344	7·1	8·5	72

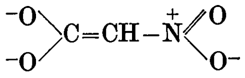


Consequently one would expect the bond between nitrogen and the central carbon atom (C_2) to be short. In fact both C_2-N (1·39 Å) and C_2-C_1 (1·38 Å) are considerably shorter than the normal single bond. This may be explained if the following two resonance forms take part in the structure:



I

and

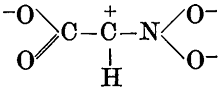


II

Taking normal single- and double-bond distances as follows:

	C–C	C–N+	N–O
Single bond	1·54	1·45	1·36
Double bond	1·33	1·23	1·15

then the bond C_1-C_2 has 52% double-bond character and C_2-N has 12% double-bond character. The resonance forms I and II therefore contribute 12% and 52% to the structure and a third form, III, must be postulated in which both C_1-C_2 and $N-C_2$ are single bonds, and this must contribute 36% to the total. The extent of the contribution of III is not surprising since both the nitro group and the carboxyl group are strongly electrophylic and will produce a tendency for an electronic drift away from the centre of the molecule. In all three resonance forms further resonance is to be expected so as to produce symmetrical carboxyl and nitro groups. Inspection of Fig. 2 shows, however, that the anion is bent in the form of the letter U and that two oxygen atoms, one from the carboxyl and the other from the nitro group, are in close proximity. Any shortening of the bonds between these two oxygen atoms and the rest of the anion will make them approach even more closely. It is reasonable to suppose therefore that the resonance within the anion which sets up symmetrical groups will be inhibited so that the bonds to the two oxygens may be kept as long as possible. The carboxyl group retains the greatest asymmetry (C_1-O_1 = 1·33 Å; C_1-O_2 = 1·27 Å) whilst the nitro group may be considered symmetrical within the limits of accuracy of the determination. Nevertheless, the observed distances are in accord with this hypothesis.



III

Vand, Morley & Lomer (1951) found unequal lengths in the carboxyl groups in lauric acid, two C–O and two C=O bonds of 1·38 Å and 1·17 Å, though the coordinates are not sufficiently accurate for too much emphasis to be placed on these distances. Morrison & Robertson (1949) have found that this inequality exists in saturated dicarboxylic acids:

	C–O (1)	C–O (2)
β-Succinic	1·25 Å	1·30 Å
Adipic	1·23	1·29
Sebacic	1·24	1·27
β-Glutaric	1·23	1·30

The number of salts of carboxylic acids whose structures have been elucidated and refined to a reasonable degree of accuracy is few. Zachariasen (1938) found complete resonance between the two C–O bonds in the formate group. The C–O distances are 1·27±0·01 Å and the bond angle 124°, but whether this is more common than incomplete resonance in the salts of carboxylic acids cannot be stated until the interatomic distances in more of them have been determined.

The lengths of 1·26 and 1·28 Å for the N–O bonds are longer than those normally found in the nitro group and the O–N–O bond angle of 121° is smaller. The resonance contributors in which both oxygen atoms of the nitro group carry a formal negative charge constitute 48% of the structure. This formal charge will cause a lengthening of the N–O bond and in this respect dipotassium nitroacetate is similar to pentaerythritol tetranitrate (N–O distance 1·27 Å) where formal charges also exist on the oxygen atoms of the nitro group. Calculation of the bond lengths in the nitro group for 26% double-bond character gives 1·25 Å, in reasonable agreement with the mean of the observed values 1·27 Å.

The resonance contributor III makes up 36% of the total and in this the carbon atom is positively charged. This positive charge will decrease the covalent radii of carbon and hence shorten the C–H bond.

There is only one hydrogen atom and the $C_2-H\ldots O_4$ distance of 3·13 Å is too great for hydrogen bonding to occur.

Fig. 3 is a perspective drawing of dipotassium nitroacetate and from this it can be seen that each potassium has eight near oxygen neighbours, four in the $z = 0$ plane, and four identical with those in the $z = 1$ plane. The distances are:

K_1–O_1	Two bonds of length	2·70 Å
K_1–O_3	Two bonds of length	2·81
K_1–O'_1	Two bonds of length	2·78
K_1–O'_2	Two bonds of length	2·99
K_2–O_3	Two bonds of length	2·90 Å
K_2–O_4	Two bonds of length	3·11
K_2–O'_4	Two bonds of length	2·88
K_2–O''_2	Two bonds of length	2·83

where O, O′, and O″ are oxygen atoms of different anions.

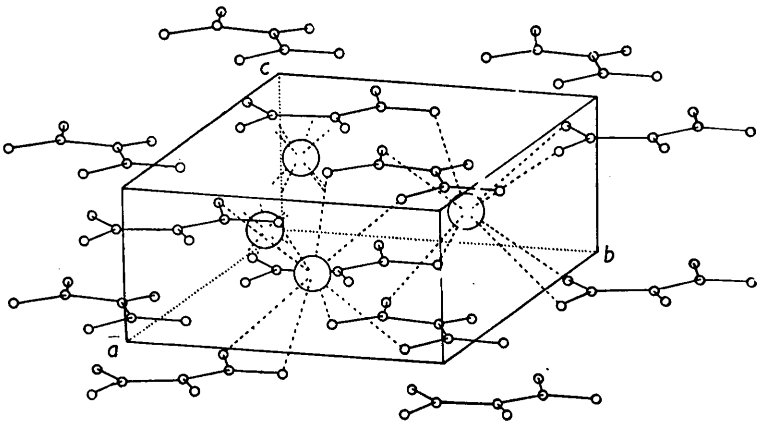


Fig. 3. Perspective drawing of the unit cell of dipotassium nitroacetate, showing the layer structure and the eightfold coordination of the potassium ions.

The potassium atoms are therefore in eightfold coordination and each oxygen atom is associated with two potassium ions. These oxygens do not form any regular arrangement in the planes where they are situated, the intramolecular distances being much shorter than the intermolecular distances.

The shortest K–O distance is 2·70 Å and, since the radius of a potassium ion in eightfold coordination is 1·37 Å, the radius of O^- is 1·33 Å. Similar potassium coordination and bonding is reported in potassium trioxalochromate (Niekerk & Schoening, 1952) and potassium bicarbonate (Nitta, Tomiie & Koo, 1952). In the former, two potassiums form eight ionic bonds of mean length 2·8 Å; in the latter, each potassium ion has eight oxygen neighbours with the K–O distances 2·68–3·13 Å.

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