

## Potassium *o*-Nitrophenolate Hemihydrate. A Refinement of the Structure Based on New Experimental Data

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The refinement of potassium *o*-nitrophenolate hemihydrate was based on three-dimensional data collected with Mo radiation (918 reflexions were observed, *i.e.* 71% of those in the range covered). The ring system of the *o*-nitrophenolate ion deviates from regular hexagon symmetry in an *o*-quinoidal mode. The ring is planar, but exocyclic atoms are out of the ring plane (by up to 0.13 Å).

### Introduction

The structure of potassium *o*-nitrophenolate hemihydrate was determined by Richards (1961), who used 460 reflexions (*h0l* and *h1l* data) for the determination. The refinement of the structure described here was made since it became useful to include phenolates in a discussion of relations between molecular structure and acidic strength (Andersen, 1971). Bush & Truter (1971) have published the molecular structure of the *o*-nitrophenolate ion in a complex formed from isonitrosoacetophenone and potassium *o*-nitrophenolate. In the final section their results are compared with those of Richards and those from the present determination.

The substance was prepared from *o*-nitrophenol and potassium hydroxide and was recrystallized from a 90% ethanol-water mixture. Crystal data for the hemihydrate are recorded in Table 1.

Table 1. *Crystal data for potassium o-nitrophenolate hemihydrate*

$C_6H_4O_3NK \cdot \frac{1}{2}H_2O$	F.W. 186.21
$Z=8$	$F(000) 760$
Monoclinic	Systematic absences
$a=24.73 \text{ \AA}^*$	$hkl: h+k=2n+1$
$b=5.21$	$h0l: l=2n+1$
$c=11.96$	Possible space groups
$\beta=105.15^\circ$	$Cc, C2/c$
	( $C2/c$ assumed)
Crystal size: $0.125 \times 0.25 \times 0.55 \text{ mm}$	
$\mu(\text{Mo } K\alpha)=6.68 \text{ cm}^{-1}$	
$D_m=1.660 (8) \text{ g cm}^{-3}$	$D_x=1.664 \text{ g cm}^{-3}$

\* Richards (1961).

The intensity data were collected on an automatic diffractometer (scintillation counter and pulse-height discriminator). Zirconium-filtered Mo  $K\alpha$  radiation was used. The intensity was recorded during a  $\theta/2\theta$  scan of  $1.6^\circ$  in  $\theta$  (scanning speed  $1.25^\circ \text{ min}^{-1}$ ), and for half the scan time at each end of the scanning interval. The 12,0,0 reflexion was measured every 15 reflexions. These measurements provided data for the calculations of scale factors for each group of 15 reflexions. These

factors were in the range 0.91–1.00. All reflexions within the range  $0.061 \leq \sin \theta/\lambda \leq 0.595$  were measured. Of the 1316 reflexions within this interval 918 had integrated intensities larger than twice their standard deviations. They were corrected for Lorentz and polarization factors and converted into structure factors. No correction for absorption was applied.

### Refinement of the structure

Structure-factor calculations based on Richards's parameters gave an  $R$  index of 0.13 (unobserved structure factors excluded from the calculations). The refinement was performed by the full-matrix least-squares program *ORFLS* of the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970). The quantity minimized was  $\sum w(F_o - F_c)^2$ . The weighting scheme was  $w = (a + F_o + bF_o^2)^{-1}$ . With  $a = 10.0$  and  $b = 0.008$  the values of  $w(F_o - F_c)^2$  were independent of  $\sin \theta$  and only slightly dependent on the magnitudes of  $F_o$ . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). No contribution from unobserved structure factors was included. The positional parameters for the five hydrogen atoms were found from difference electron-density maps.

In the final least-squares calculations 105 parameters were varied. The thermal parameters for the five hydrogen atoms were held isotropic and were not refined. They were arbitrarily set to  $3.0 \text{ \AA}^2$ . In the final cycle the average ratio parameter shift/standard deviation was 0.15 (maximum value 0.59). In this cycle the  $R$  index was 0.037 and  $R_w$  was 0.051.

The final parameters are given in Table 2.\*

### The crystal structure

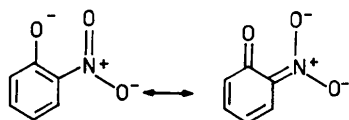
The crystal structure is shown in Fig. 1, which gives the content of one unit cell.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30634 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The structure is composed of layers of *o*-nitrophenolate ions parallel to the (100) plane. Each of the layers is on the side facing the planes  $x=0$  and  $x=0.5$  linked to another layer by hydrogen bonds and by ionic bonds involving the potassium ion and the oxygen atoms of the phenolate ions. This arrangement of bonds between two layers across the planes  $x=0$  and  $x=0.5$  is shown in the central part of Fig. 1. The hydrogen bonds have water molecules as donors and O(1) atoms as acceptors and are 2.769 Å long. The ionic bonds are shown in detail in Fig. 2. The composite layers (double layers) formed by these bonds are bonded to other composite layers by van der Waals forces only. This arrangement gives rise to the predominant cleavage along (100).

### Molecular structure

Bond distances are given in Fig. 3. The mean C–C bond length in the *o*-nitrophenolate ion is 1.400 Å with a standard deviation of 0.028 Å. This is four times the standard deviation of the individual C–C bond lengths and hence a separation of the bonds into two groups, the one with four bonds longer than 1.39 Å, the other with two bonds shorter than 1.38 Å, is justified. Similar mean C–C distances and standard deviations have been found in the *o*-nitrophenolate ion by Bush & Truter (1971) who interpret this in terms of resonance with contributions from the following structures:



This is consistent with the observation that C(6)–C(1), C(1)–C(2), C(2)–C(3) and C(4)–C(5) are long and C(3)–C(4) and C(5)–C(6) are short.

Table 3 shows a comparison between bond lengths and angles found in three determinations of the struc-

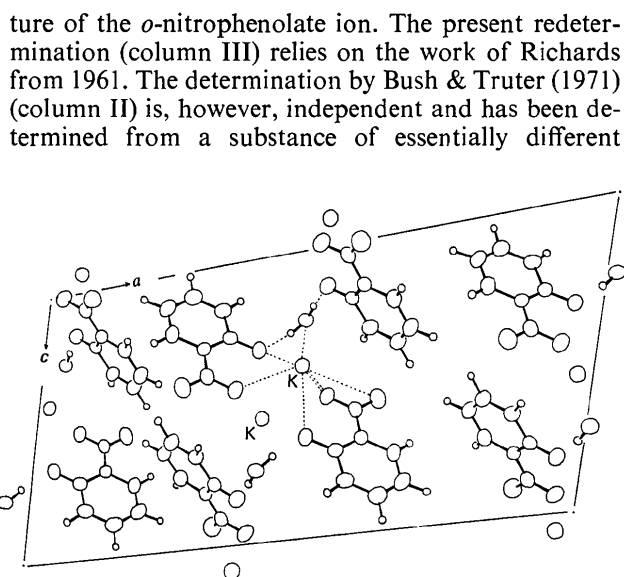


Fig. 1. The structure viewed down the *b* axis. Dashed lines represent the hydrogen bonds or ionic bonds.

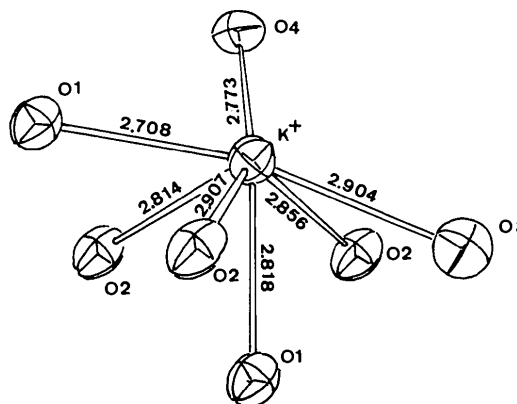


Fig. 2. The surroundings of the potassium ion.

Table 2. *Final atomic parameters and standard deviations*

For numbering of atoms see Fig. 3. Positional parameters ( $\times 10^4$ ) and thermal parameters (in the form  $[-\frac{1}{4} \sum \sum B_{ij} h_i h_j a_i^* a_j^*]$ ) are given.

	<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>	416 (1)	−1839 (2)	−771 (1)	3.40 (04)	3.21 (04)	3.18 (04)	−0.22 (04)	0.64 (03)	−0.18 (04)
O(1)	540 (1)	−871 (6)	1602 (3)	3.26 (13)	3.92 (15)	3.83 (14)	−0.49 (12)	0.49 (11)	0.67 (13)
O(2)	602 (1)	3216 (7)	291 (3)	3.71 (14)	4.05 (16)	3.78 (14)	−0.74 (13)	−0.15 (11)	0.78 (13)
O(3)	1370 (1)	5325 (7)	612 (3)	4.50 (16)	4.35 (17)	5.40 (18)	−1.04 (15)	1.37 (14)	0.83 (14)
O(4)	0	−4705 (8)	2500	4.36 (21)	3.22 (20)	2.76 (17)		0.78 (15)	
N(1)	1090 (1)	3586 (8)	894 (3)	3.08 (16)	3.65 (19)	3.65 (16)	−0.24 (15)	1.18 (13)	−0.42 (15)
C(1)	1024 (2)	−98 (9)	2180 (3)	3.29 (18)	3.48 (20)	2.66 (18)	0.47 (17)	0.87 (15)	−0.19 (15)
C(2)	1319 (2)	2031 (9)	1881 (3)	2.94 (17)	3.60 (20)	2.64 (16)	0.19 (17)	0.62 (14)	−0.28 (17)
C(3)	1857 (2)	2743 (10)	2539 (4)	3.03 (19)	5.15 (27)	4.18 (21)	−0.49 (19)	0.81 (16)	−0.88 (20)
C(4)	2107 (2)	1387 (13)	3525 (4)	3.43 (21)	7.15 (35)	3.94 (22)	0.66 (24)	−0.29 (18)	−0.80 (24)
C(5)	1826 (2)	−687 (12)	3856 (4)	4.24 (24)	5.94 (31)	3.66 (22)	1.41 (23)	0.35 (18)	0.36 (22)
C(6)	1309 (2)	−1431 (10)	3221 (4)	4.17 (21)	4.56 (26)	3.00 (18)	0.85 (20)	0.75 (16)	0.38 (19)
H(1)	180	−3550	2100	3.00	3.00	3.00		0.77	
H(3)	2040	4330	2300						
H(4)	2510	1900	3960						
H(5)	2010	−1920	4650						
H(6)	1130	−3230	3520						

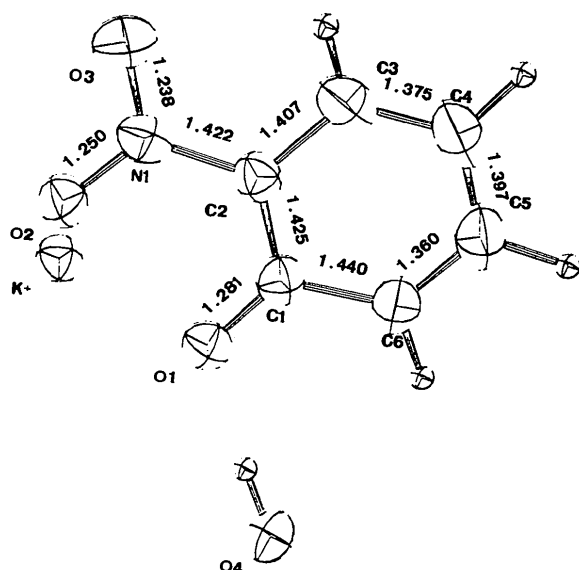


Fig. 3. Perspective drawing of the asymmetric unit in potassium *o*-nitrophenolate hemihydrate. Atoms are represented by ellipsoids enclosing 50% of the thermal displacements.

composition (the 1:1 complex between isonitrosoacetophenone and potassium *o*-nitrophenolate). The determinations are seen to agree within the estimated standard deviations.

Table 3. Bond lengths (Å) and angles (°) in the *o*-nitrophenolate ion (estimated standard deviations in parentheses)

For the numbering of atoms see Fig. 3.

	I Richards (1961)	II Bush & Truter (1971)	III This investi- gation
C(1)–C(2)	1.46 (5)	1.421 (6)	1.425 (7)
C(2)–C(3)	1.42 (4)	1.393 (6)	1.407 (6)
C(3)–C(4)	1.40 (4)	1.347 (7)	1.375 (7)
C(4)–C(5)	1.29 (5)	1.383 (7)	1.397 (9)
C(5)–C(6)	1.38 (4)	1.372 (7)	1.360 (7)
C(6)–C(1)	1.43 (4)	1.414 (6)	1.440 (6)
C(1)–O(1)	1.26 (3)	1.298 (5)	1.281 (5)
C(2)–N	1.39 (4)	1.433 (5)	1.422 (5)
N—O(2)	1.26 (3)	1.230 (4)	1.250 (4)
N—O(3)	1.17 (3)	1.224 (4)	1.238 (5)
O(1)–C(1)–C(2)	126 (2)	124.3 (4)	125.3 (4)
O(1)–C(1)–C(6)	121 (3)	121.0 (4)	119.5 (4)
C(2)–C(1)–C(6)	113 (2)	114.7 (4)	115.2 (4)
C(1)–C(2)–C(3)	122 (2)	121.7 (4)	122.5 (4)
C(1)–C(2)–N	122 (2)	121.2 (4)	122.2 (3)
C(3)–C(2)–N	116 (3)	117.1 (4)	115.3 (4)
C(2)–C(3)–C(4)	118 (3)	121.2 (5)	119.5 (5)
C(3)–C(4)–C(5)	122 (2)	119.3 (5)	119.6 (4)
C(4)–C(5)–C(6)	122 (3)	120.9 (5)	121.8 (5)
C(2)–N—O(2)	118 (2)	120.1 (3)	120.4 (4)
C(2)–N—O(3)	120 (2)	120.0 (3)	120.8 (3)
O(2)–N—O(3)	122 (2)	119.8 (4)	118.7 (3)

Another interesting feature is that in all three determinations the O(1)–C(1)–C(2) angle is significantly

larger than the O(1)–C(1)–C(6) angle. This is probably due to the short near-contact distance of 2.672 Å between O(1) and O(2) as has been suggested by Bush & Truter.

The deviations of the atoms of the phenolate ion from various planes through the ion are given in Table 4. From this table one concludes that the carbon ring and nitro group are both planar. The nitro group, however, does not lie in the plane of the carbon ring. It is bent out of the ring plane and twisted around the C–N bond by 4.65°. This is found in other structures where nitro groups are in the *ortho* position to phenolate oxygen atoms and is probably due to a slight overcrowding. The phenolate oxygen O(1) is out of the molecular plane in the opposite direction to the adjacent nitro group oxygen O(2). This may be taken as further evidence of molecular overcrowding.

Table 4. Deviations (Å) of atoms from planes through the *o*-nitrophenolate ion

Plane I	$14.299x - 3.186y - 8.043z = -0.264$
Plane II	$14.264x - 3.165y - 8.108z = -0.290$
Plane III	$12.619x - 3.351y - 8.185z = -0.556$

(a) Deviations of atoms included in the plane calculation

I	II	III
C(1)	0.006	C(1) 0.014
C(2)	-0.009	C(2) 0.002
C(3)	0.005	C(3) 0.013
C(4)	0.003	C(4) 0.001
C(5)	-0.006	C(5) -0.014
C(6)	0.002	C(6) -0.001
		N -0.015
		O(2) 0
		O(3) 0

(b) Deviations of atoms not included in the plane calculation

I	II	III
N	-0.038	N 0.002
O(1)	0.025	O(1) 0.036
O(2)	-0.134	O(2) -0.105
O(3)	0.035	O(3) 0.062
H(3)	-0.06	H(3) -0.05
H(4)	-0.03	H(4) -0.03
H(5)	-0.04	H(5) -0.06
H(6)	0.01	H(6) -0.01

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