3-Hydroxy-4-nitro-6*H*-1,2,6-thiadiazine 1,1-Dioxide: Sodium and Potassium Salts

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Abstract

The title compounds form part of a series of *S*-dioxo analogs of pyrimidines which could act as potential antimetabolites. $C_3H_2N_3O_5S^-.Na^+.H_2O$ was refined to $R = 0.041$ using 1945 independent reflexions; monoclinic, space group $P2_1/c$ with $Z = 4$, $a = 6.2914$ (3), $b = 14.001$ (1), $c = 8.9204$ (3) Å, $\beta = 95.382$ (4)°. The refinement for $C_3H_2N_3O_5S^-.K^+.H_2O$ led to $R = 0.039$ for 2006 reflexions; monoclinic, space group $P2_1/c$ with $Z = 4$, $a = 6.0744$ (4), $b = 18.533$ (2), $c = 7.497$ (1) Å, $\beta = 91.68$ (1)°. The anion, formed by deprotonation of the title compound, acts as a bidentate ligand for Na^+ ions giving rise to two identical $Na–O$ bonds of 2.40 Å. In the potassium salt, however, those $K–O$ distances are unequal, 2.88 and 3.17 Å (10% elongated) and so the anion seems to behave as a monodentate ligand. The Na^+ ions are octahedrally coordinated, with distances ranging from 2.34 to 2.49 Å. The K^+ ions are mainly surrounded by seven neighbours at distances in the range 2.78 to 3.01 Å, forming a laterally capped trigonal prism. The observed $Na–O$ bond lengths agree with the expected distances for an interaction model of cation–dipole type. The observed $K–O$ distances are, however, elongated 7% with respect to the expected ones. These observations could be related to the different cationic changeability presented by these compounds. Strong electron modifications are found within the thiadiazine rings of these salts when compared with the free heterocyclic compound. Proton migration occurs within the thiadiazine rings during the formation of both salts. Dimeric anions are formed through two centrosymmetric hydrogen bonds.

Introduction

The compounds whose crystal structures are reported correspond respectively to the monohydrated salts of sodium (hereafter abbreviated to 4NO2-NA) and potassium (4NO2-K) of the anion formed by deprotonation of the hydroxy function of 3-hydroxy-4-nitro-6*H*-1,2,6-thiadiazine 1,1-dioxide (4NO2). The crystal structure of the free heterocyclic compound (4NO2)

is reported in this journal (Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982). All these compounds, synthesized by Goya & Stud (1978), form part of a series of analogues of pyrimidines which could act as potential antimetabolites.

It is interesting to point out that 4NO2, prepared with sodium ethoxide, binds Na^+ ions giving rise to 4NO2-NA, and that this binding occurs in such a way that neither acid treatment nor resin exchange could release 4NO2. On the other hand, the K^+ ions in 4NO2-K can be exchanged to give the free heterocyclic compound 4NO2.

Experimental

4NO2-NA and 4NO2-K were crystallized from aqueous solutions as transparent single crystals (colourless and pale yellow, respectively). Lattice parameters given in the *Abstract* were obtained by the procedure reported in 4NO2 using 35 reflexions in each case. Other crystal data for 4NO2-NA (and 4NO2-K) are: $D_c = 1.98$ Mg m^{-3} (1.82 Mg m^{-3}), crystal dimensions $0.32 \times 0.17 \times 0.10$ mm ($0.30 \times 0.20 \times 0.14$ mm), $\mu = 0.483$ mm^{-1} (0.875 mm^{-1}) for $\lambda = 0.71069$ Å, θ limits 2–32° (2–35°), number of unique reflexions collected: 2668 (3715), observed reflexions used with $I > 2\sigma(I)$: 1945 (2006). X-ray intensities were collected and reduced to F_{rel} values as described for 4NO2 (Esteban-Calderón *et al.*, 1982).

Scattering factors for neutral atoms and anomalous-dispersion corrections for S, Na and K were taken from *International Tables for X-ray Crystallography* (1974). The interpretation of the corresponding Patterson maps for 4NO2-NA and 4NO2-K gave the positions of the heavy atoms. Successive Fourier syntheses revealed the remaining atoms of the structures. The location of the H atoms and the weighted refinements were performed in a similar way as described for 4NO2 (Esteban-Calderón *et al.*, 1982). The number of reflexions per variable used in the refinements was 14 in each case. The final unweighted and weighted disagreement indices are $R = 0.041$, $R_w = 0.042$ (4NO2-NA) and R

Table 1. *Atomic coordinates and isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *for* $4NO_2\text{-NA}$

$$U_{eq} = \tfrac{1}{3} \textstyle\sum_i \textstyle\sum_j a_i^* a_j^* (\mathbf{a}_i . \mathbf{a}_j).$$

	x	y	z	U_{eq}
S	0·26433 (8)	0·33766 (4)	0·72348 (5)	23
C(1)	0·58400 (31)	0·33321 (16)	0·57634 (23)	24
C(2)	0·47493 (28)	0·37528 (14)	0·44901 (20)	19
C(3)	0·27340 (29)	0·42362 (13)	0·45559 (20)	18
N(1)	0·51318 (29)	0·31976 (14)	0·70845 (21)	29
N(2)	0·19264 (28)	0·41793 (13)	0·59385 (19)	24
N(3)	0·58838 (26)	0·38284 (13)	0·31903 (19)	22
O(1)	0·14692 (31)	0·25183 (13)	0·68954 (24)	40
O(2)	0·23788 (35)	0·38076 (15)	0·86523 (19)	42
O(3)	0·17848 (23)	0·47400 (11)	0·35712 (16)	24
O(4)	0·77869 (24)	0·36107 (13)	0·32754 (20)	34
O(5)	0·49396 (25)	0·41165 (13)	0·19905 (18)	31
O(6)	−0·21240 (27)	0·42583 (14)	−0·02803 (20)	33
Na	0·12300 (15)	0·40958 (7)	0·10616 (10)	30

				U
H(C1)	0·720 (5)	0·312 (2)	0·570 (3)	0 (6)
H(N2)	0·078 (7)	0·454 (3)	0·606 (4)	25 (9)
H1(O6)	−0·304 (8)	0·425 (3)	0·036 (5)	35 (11)
H2(O6)	−0·260 (7)	0·394 (3)	−0·103 (5)	29 (10)

Table 2. *Atomic coordinates and isotropic temperature factors* $(\text{Å}^2 \times 10^3)$ *for* $4NO_2\text{-K}$

$$U_{eq} = \tfrac{1}{3} \textstyle\sum_i \textstyle\sum_j a_i^* a_j^* (\mathbf{a}_i . \mathbf{a}_j).$$

	x	y	z	U_{eq}
S	0·27423 (9)	0·35984 (3)	0·19101 (7)	26
C(1)	−0·06368 (38)	0·42832 (14)	0·28209 (33)	30
C(2)	0·02983 (36)	0·49532 (12)	0·25231 (30)	26
C(3)	0·22975 (36)	0·50408 (11)	0·15556 (28)	24
N(1)	0·02466 (35)	0·36460 (12)	0·25249 (33)	34
N(2)	0·32892 (35)	0·43966 (10)	0·11093 (30)	29
N(3)	−0·09606 (38)	0·55745 (12)	0·29784 (28)	33
O(1)	0·28971 (40)	0·30962 (11)	0·04659 (31)	45
O(2)	0·41806 (38)	0·34526 (15)	0·33959 (31)	49
O(3)	0·30754 (31)	0·56099 (9)	0·10012 (26)	33
O(4)	−0·29072 (36)	0·54883 (14)	0·33400 (37)	53
O(5)	−0·00943 (48)	0·61713 (12)	0·30303 (38)	56
O(6)	0·19639 (36)	0·75358 (13)	0·53897 (32)	41
K	0·47096 (11)	0·68364 (3)	0·29905 (7)	36

				U
H(C1)	−0·210 (6)	0·427 (2)	0·342 (5)	13 (8)
H(N2)	0·434 (6)	0·442 (2)	0·042 (5)	7 (7)
H1(O6)	0·117 (10)	0·727 (3)	0·581 (8)	54 (17)
H2(O6)	0·099 (10)	0·783 (3)	0·505 (8)	50 (15)

= 0·039, R_w = 0·050 (4NO2-K). The atomic parameters are shown in Tables 1 and 2 respectively.*

Description and discussion of the structures

Figs. 1 and 2 show partial views of the crystal structures of 4NO2-NA and 4NO2-K respectively.

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* Lists of coefficients for the weighting schemes, structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36460 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
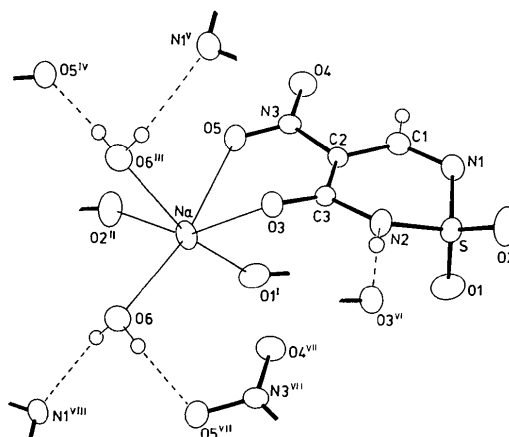

Fig. 1. Perspective drawing (Johnson, 1965) of 4NO2-NA. Some symmetrically related atoms are also shown. For symmetry operations, see Table 3. Thermal ellipsoids scaled to 50% probability.
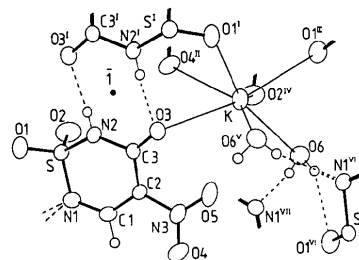

Fig. 2. Perspective drawing (Johnson, 1965) of 4NO2-K. Some symmetrically related atoms are also shown. For symmetry operations, see Table 3. Thermal ellipsoids scaled to 50% probability.

Some symmetrically related atoms are also shown for clarity and hydrogen bonds are represented by dashed lines.

Each structure contains one crystallographically independent water molecule, which forms part of the coordination sphere of the cations, and is involved in the hydrogen-bond schemes (Figs. 1 and 2). Both structures contain dimeric thiadiazine molecules formed through two centrosymmetric $N(2)–H\cdots O(3)$ intermolecular hydrogen bonds (Fig. 2). This situation is not shown in Fig. 1 for reasons of clarity. Table 3 shows the geometrical features of the intermolecular contacts for 4NO2-NA and 4NO2-K, where an asymmetrically bifurcated hydrogen bond (Rich & Davidson, 1968) is found.

Table 4 shows a comparison of the bond lengths for 4NO2-NA and 4NO2-K. Table 5 contains a similar comparison for bond angles. The magnitudes of the bond lengths within the common part of the molecular rings of both compounds are found to be very similar. In fact, a half-normal probability plot (Abrahams & Keve, 1971) calculated with these distances gives a

Table 3. *Intermolecular contacts with e.s.d.'s in parentheses*

$X–H\cdots Y$	$X\cdots Y$	$X–H$	$H\cdots Y$	$X–H\cdots Y$
Hydrogen bonds for 4NO2-NA				
$N(2)–H\cdots O(3^{vi})$	2·850 (2) Å	0·89 (4) Å	1·96 (4) Å	176 (4)°
$O(6)–H(1)\cdots O(5^{vii})$	2·874 (2)	0·85 (5)	2·03 (5)	174 (4)
$O(6)–H(2)\cdots N(1^{viii})$	3·154 (3)	0·83 (5)	2·35 (4)	164 (4)
Hydrogen bonds for 4NO2-K				
$N(2)–H\cdots O(3^i)$	2·754 (3) Å	0·83 (4) Å	1·93 (4) Å	174 (3)°
$O(6)–H(1)\cdots N(1^{vii})$	3·028 (3)	0·77 (6)	2·29 (6)	163 (6)
$*O(6)–H(2)\cdots O(1^{vi})$	3·178 (3)	0·84 (6)	2·43 (6)	149 (5)
$*O(6)–H(2)\cdots N(1^{vi})$	3·262 (3)	0·84 (6)	2·55 (6)	144 (5)

Other contacts for 4NO2-NA		Other contacts for 4NO2-K	
$Na\cdots O(4^{vii})$	3·139 (2)	$O(3)\cdots O(4^{ii})$	2·971 (3)
$Na\cdots C(3)$	3·177 (2)	$C(1)\cdots O(3^{viii})$	3·193 (3)
$Na\cdots N(3)$	3·358 (2)	$K\cdots O(5)$	3·169 (3)
$Na\cdots Na^{iii}$	3·441 (1)	$K\cdots O(2^{iii})$	3·248 (3)
$O(5)\cdots O(6^{ix})$	2·874 (2)	$K\cdots O(5^{ii})$	3·388 (3)
$O(3)\cdots O(4^{vii})$	2·962 (2)		
$O(3)\cdots C(1^x)$	3·115 (3)		

Symmetry operations

	4NO2-NA			4NO2-K	
(i)	$x,$	$\frac{1}{2}–y, -\frac{1}{2}+z$		$1–x,\ 1–y,$	$–z$
(ii)	$x,$	$y, -1+z$		$1+x,\ \ y,$	z
(iii)	$–x,$	$1–y, \ \ –z$		$1–x,\ \frac{1}{2}+y,$	$\frac{1}{2}–z$
(iv)	$1–x,$	$1–y, \ \ –z$		$1–x,\ 1–y,$	$1–z$
(v)	$1–x,$	$1–y, \ 1+z$		$x,\ \frac{1}{2}–y,$	$-\frac{1}{2}+z$
(vi)	$–x,$	$1–y, \ 1–z$		$–x,\ \frac{1}{2}+y,$	$\frac{1}{2}–z$
(vii)	$-1+x,$	$y, \ \ \ z$		$–x,\ 1–y,$	$1–z$
(viii)	$-1+x,$	$y, -1+z$		$–x,\ 1–y,$	$-z$
(ix)	$1+x,$	$y, \ \ \ z$			
(x)	$1–x,$	$1–y, \ 1–z$			

* Bifurcated hydrogen bond.

Table 4. *Bond lengths (Å) with e.s.d.'s in parentheses*

See Table 3 for symmetry operations.

	4NO2-NA	4NO2-K
S–O(1)	1·428 (2)	1·433 (2)
S–O(2)	1·425 (2)	1·421 (2)
S–N(1)	1·603 (2)	1·600 (2)
S–N(2)	1·645 (2)	1·634 (2)
N(1)–C(1)	1·312 (3)	1·319 (3)
C(1)–C(2)	1·401 (3)	1·386 (3)
C(1)–H	0·91 (3)	1·01 (4)
C(2)–C(3)	1·443 (3)	1·442 (3)
C(2)–N(3)	1·421 (3)	1·429 (3)
C(3)–N(2)	1·380 (3)	1·383 (3)
C(3)–O(3)	1·236 (2)	1·233 (3)
N(2)–H	0·89 (4)	0·83 (4)
N(3)–O(4)	1·231 (2)	1·231 (3)
N(3)–O(5)	1·242 (2)	1·225 (3)
O(6)–H(1)	0·85 (5)	0·77 (6)
O(6)–H(2)	0·83 (5)	0·84 (6)

	4NO2-NA		4NO2-K
Na–O(6)	2·337 (2)	K–O(6^v)	2·783 (2)
Na–O(2^{ii})	2·366 (2)	K–O(6)	2·806 (2)
Na–O(1^i)	2·380 (2)	K–O(2^{iv})	2·824 (2)
Na–O(5)	2·402 (2)	K–O(3)	2·879 (2)
Na–O(3)	2·408 (2)	K–O(4^{ii})	2·896 (3)
Na–O(6^{iii})	2·487 (2)	K–O(1^{iii})	2·967 (2)
		K–O(1^i)	3·011 (2)

Table 5. *Bond angles (°) with e.s.d.'s in parentheses*

See Table 3 for symmetry operations.

	4NO2-NA	4NO2-K
O(1)–S–O(2)	116·3 (1)	114·6 (1)
O(1)–S–N(1)	109·9 (1)	109·7 (1)
O(1)–S–N(2)	108·9 (1)	107·0 (1)
O(2)–S–N(1)	109·7 (1)	110·5 (1)
O(2)–S–N(2)	106·7 (1)	109·5 (1)
N(1)–S–N(2)	104·7 (1)	105·1 (1)
S–N(1)–C(1)	118·0 (2)	119·5 (2)
S–N(2)–C(3)	124·6 (1)	126·7 (2)
S–N(2)–H	118 (3)	116 (2)
C(3)–N(2)–H	117 (3)	117 (2)
C(2)–N(3)–O(4)	119·4 (2)	118·2 (2)
C(2)–N(3)–O(5)	119·4 (2)	120·2 (2)
O(4)–N(3)–O(5)	121·2 (2)	121·6 (3)
N(1)–C(1)–C(2)	127·4 (2)	127·2 (2)
N(1)–C(1)–H	114 (2)	115 (2)
C(2)–C(1)–H	118 (2)	117 (2)
C(1)–C(2)–C(3)	122·0 (2)	122·5 (2)
N(3)–C(2)–C(1)	116·6 (2)	117·3 (2)
N(3)–C(2)–C(3)	120·6 (2)	119·6 (2)
N(2)–C(3)–O(3)	118·3 (2)	118·9 (2)
C(2)–C(3)–N(2)	114·1 (2)	113·8 (2)
C(2)–C(3)–O(3)	127·3 (2)	127·1 (2)
H(1)–O(6)–H(2)	109 (4)	96 (6)

	4NO2-NA		4NO2-K
O(3)–Na–O(5)	67·9 (1)	O(6)–K–O(6^v)	84·3 (1)
O(3)–Na–O(6^{iii})	84·1 (1)	O(6)–K–O(3)	119·6 (1)
O(3)–Na–O(2^{ii})	151·5 (1)	O(6)–K–O(4^{ii})	130·2 (1)
O(3)–Na–O(6)	119·0 (1)	O(6)–K–O(1^i)	147·5 (1)
O(3)–Na–O(1^i)	93·8 (1)	O(6)–K–O(1^{iii})	71·4 (1)
O(5)–Na–O(6^{iii})	81·2 (1)	O(6)–K–O(2^{iv})	66·6 (1)
O(5)–Na–O(2^{ii})	86·9 (1)	O(6^v)–K–O(3)	77·1 (1)
O(5)–Na–O(6)	167·6 (1)	O(6^v)–K–O(4^{ii})	135·4 (1)
O(5)–Na–O(1^i)	82·7 (1)	O(6^v)–K–O(1^i)	71·0 (1)
O(6^{iii})–Na–O(2^{ii})	78·9 (1)	O(6^v)–K–O(1^{iii})	102·8 (1)
O(6^{iii})–Na–O(6)	89·1 (1)	O(6^v)–K–O(2^{iv})	150·8 (1)
O(6^{iii})–Na–O(1^i)	163·4 (1)	O(3)–K–O(4^{ii})	61·9 (1)
O(2^{ii})–Na–O(6)	83·7 (1)	O(3)–K–O(1^i)	75·8 (1)
O(2^{ii})–Na–O(1^i)	96·1 (1)	O(3)–K–O(1^{iii})	168·7 (1)
O(6)–Na–O(1^i)	106·3 (1)	O(3)–K–O(2^{iv})	114·6 (1)
		O(4^{ii})–K–O(1^i)	82·0 (1)
		O(4^{ii})–K–O(1^{iii})	113·9 (1)
		O(4^{ii})–K–O(2^{iv})	69·2 (1)
		O(1^i)–K–O(1^{iii})	93·4 (1)
		O(1^i)–K–O(2^{iv})	136·5 (1)
		O(1^{iii})–K–O(2^{iv})	71·0 (1)

linear array with slope 2·7 (2), zero intercept at −0·2 (2) and a correlation coefficient of the fit of 0·98.

Some electron delocalization within the ring of each compound can be deduced from an inspection of the bond distances (Table 4). This can be explained assuming some non-integer bond orders, as commonly occurs for most thiadiazine compounds (Esteban-Calderón *et al.*, 1982; Cabezuelo, Cano, Foces-Foces & Garcia-Blanco, 1977). From these bond lengths and from the above-mentioned similarity we propose the major electron distributions shown in Fig. 3, according to Linnett's (1966) model. By comparing these electron-distribution models with the one which can be
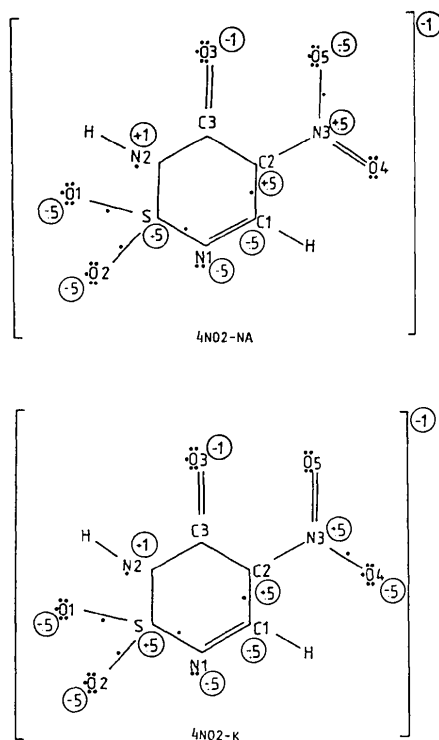
Fig. 3. Major electron distributions for 4NO2-NA and 4NO2-K.

Table 6. *Torsion angles* (°) *with e.s.d.'s in parentheses*

	4NO2-NA	4NO2-K
N(2)–S–N(1)–C(1)	−28·0 (2)	−20·3 (2)
S–N(1)–C(1)–C(2)	10·3 (3)	5·7 (3)
N(1)–C(1)–C(2)–C(3)	9·7 (3)	10·3 (3)
C(1)–C(2)–C(3)–N(2)	−4·7 (2)	−5·8 (3)
C(2)–C(3)–N(2)–S	−19·7 (2)	−14·0 (3)
C(3)–N(2)–S–N(1)	34·7 (2)	25·9 (2)
C(1)–C(2)–N(3)–O(5)	173·7 (2)	167·8 (2)
C(1)–C(2)–N(3)–O(4)	−6·7 (2)	−11·1 (3)
O(3)–C(3)–C(2)–N(3)	0·2 (2)	−2·1 (3)
C(3)–C(2)–N(3)–O(5)	−16·8 (2)	−21·1 (3)

Table 7. *Atomic deviations* (Å) *from least-squares planes* (*Nardelli, Musatti, Domiano & Andreetti,* 1965) *with e.s.d.'s in parentheses*

Atoms marked with asterisks are not included in the calculations.

Plane 1	4NO2-NA	4NO2-K
C(1)	−0·049 (2)	−0·046 (3)
C(2)	0·027 (2)	0·032 (2)
C(3)	−0·003 (2)	−0·009 (2)
N(1)	0·024 (2)	0·024 (2)
N(2)	−0·008 (2)	−0·004 (2)
*S	0·470 (1)	0·357 (1)
*O(3)	−0·127 (2)	−0·142 (2)
*N(3)	−0·099 (2)	−0·045 (2)
*O(4)	−0·388 (2)	−0·381 (3)
*O(5)	0·078 (2)	0·239 (3)

Plane 2	4NO2-NA	4NO2-K
O(3)	−0·049 (2)	−0·059 (2)
C(3)	0·055 (2)	0·064 (2)
C(2)	0·042 (2)	0·032 (2)
N(3)	−0·109 (2)	−0·117 (2)
O(5)	0·084 (2)	0·166 (3)
*O(4)	−0·433 (2)	−0·511 (3)
*Na	−0·702 (1)	−
*K	−	1·650 (1)

	4NO2-NA	4NO2-K
Angle between planes 1/2	1·7 (4)°	3·3 (4)°

deduced for the free compound 4NO2 (Esteban-Calderón *et al.*, 1982), strong electron modifications are observed within the thiadiazine ring, when Na⁺ or K⁺ ions are attached to it. The main modifications occur around O(3), C(3), N(2), S and N(1).

Another interesting fact is that in the salt-formation reaction, *i.e.* in the synthesis of 4NO2-NA or 4NO2-K from 4NO2, one of the H atoms, either the one attached to O(3) or that attached to N(1) (see Fig. 1 in 4NO2, Esteban-Calderón *et al.*, 1982), migrates to the N(2) atom (Fig. 3). This fact, together with the positive formal charge assumed on N(2), justifies the regio-selective alkylation of these 1,2,6-thiadiazine 1,1-dioxide derivatives. Methylation of 4NO2 in sodium or potassium hydroxide leads only to the N(2)-methyl derivative (Goya, Martínez, Ochoa & Stud, 1981).

Table 6 shows a comparison of some torsion angles for 4NO2-NA and 4NO2-K. Table 7 shows the atomic deviations from several least-squares planes. The thiadiazine ring in both compounds is in the envelope conformation, the S atom being at the flap. According to a conformational model for a six-membered ring (Cano, Foces-Foces & García-Blanco, 1977), these rings can be described as 2,4-diplanar.

The Na⁺ ion in 4NO2-NA is mainly surrounded by six O atoms (Fig. 1). Two of these O atoms belong to the bidentate ligand and form two Na—O bonds of almost identical length (2·402 and 2·408 Å); this

results in a non-planar six-membered ring, the Na⁺ ion being 0·72 Å out of the plane of the other five atoms (Table 7). The nitro group is twisted 1·6° from the plane of the thiadiazine ring. Two more O atoms, of O(1) and O(2) type, and two equivalent water molecules, O(6), form a somewhat distorted octahedron around Na⁺ (Fig. 1 and Table 4). A seventh O atom, O(4ᵛⁱⁱ) (Fig. 1), approaches Na⁺ with a distance of 3·139 Å, elongated 31% with respect to the average of the other Na—O bonds. The bond angles around the Na⁺ ion are shown in Table 5.

The K⁺ ion in 4NO2-K has mainly seven neighbouring O atoms at distances ranging from 2·783 to 3·011 Å (Fig. 2, Tables 4 and 5). Six are located at the

Table 8. *Ionic and van der Waals radii* (Å)

Na^+	0·97	*Handbook of Chemistry and Physics* (1977)
K^+	1·33	
O	1·40	Bondi (1964)

corners of a somewhat distorted trigonal prism, the seventh O atom being located on the normal to one of the side faces. An eighth O atom, O(5) of the bidentate ligand (Fig. 2), is at 3·169 Å from K^+, which represents an elongation of ~10% with respect to the other seven K—O distances, and probably still contributes to a smaller extent to the bonding.

4NO2 (Estaban-Calderón *et al.*, 1982), considered as an anion, carries additional neutral donor sites, so that as a ligand it becomes more powerful and acts as a charge neutralizer as well as serving to satisfy the cationic coordination requirements. Moreover, the charge of this mononegative anion is distributed through delocalization of its bonds (Fig. 3), producing an increase of its capability as a ligand. On the other hand, the general rule that the cation–anion interaction increases with the charge density of the cation (Poonia & Bajaj, 1979) is clearly observed in 4NO2-NA and 4NO2-K. In fact, Na^+ is surrounded by four anionic sites (Fig. 1), whereas K^+ is bonded to five anionic sites (Fig. 2), and in both cases Na^+ and K^+ neutralize the same negative total charge. From this, one can deduce a higher intensity of interaction in Na—O than in K—O bonds, which can be evaluated in terms of the observed Na—O and K—O bond lengths. In fact, taking the ionic and van der Waals radii given in Table 8, and assuming an interaction model of cation–dipole type, the following expected distances are obtained: Na^+—O = 2·37, K^+—O = 2·73 Å. The mean distance between the cation and anion sites observed in 4NO2-NA only exceeds the expected value by 0·8%, whereas in 4NO2-K the mean observed values are elongated 6·8% with respect to the expected ones. These observations can be connected with the different cationic changeability presented by 4NO2-NA and 4NO2-K, as

mentioned above. However, it still remains unclear whether this different behaviour is a consequence of the fact that Na^+ interacts strongly with the bidentate ligand, with two identical short Na—O bonds, which is not observed in the case of the K^+ ion (Figs. 1 and 2).

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4-Cyano-3-hydroxy-6H-1,2,6-thiadiazine 1,1-Dioxide: Sodium and Potassium Salts

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Abstract

These compounds belong to a series of *S*-dioxo analogs of pyrimidines synthesized as potential antimetab-olites. $C_4H_2N_3O_3S^-.Na^+.2H_2O$ has been refined to R = 0·035 with 2672 independent reflexions; triclinic, space group $P\bar{1}$ with Z = 2, a = 10·384 (1), b = 7·138 (1), c = 6·305 (1) Å, α = 108·65 (1), β =

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