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Potassium *p*-nitrophenyl sulfate

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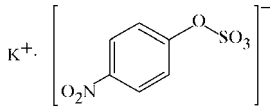
The crystal structure of the title compound, $K^+ \cdot C_6H_4NO_6S^-$, is built up from *p*-nitrophenyl sulfate anions and potassium cations. Adjacent anions form dimers, which are linked together in a three-dimensional network *via* short C—H···O contacts. The coordination sphere of the K^+ ions may be described as a distorted square antiprism. The crystal structure is further stabilized by π–π stacking interactions between the aryl rings.

Comment

p-Nitrophenyl sulfate (pNPS) is one of the synthetic compounds commonly used as a substrate in a wide range of biochemical assays (Dodgson *et al.*, 1956) utilizing various hydrolase (EC 3.1) and sulfotransferase (EC 2.8.2) enzymes. In hydrolase assays, pNPS serves as a substrate for enzymes, mainly sulfatases (EC 3.1.6.1) (Suiko *et al.*, 1996). It is also well recognized that pNPS can be hydrolyzed by numerous alkaline phosphatases (EC 3.1.3.1; O'Brien & Herschlag, 2001). This phenomenon, as well as the level of structural homology of the above-mentioned enzymes (Bond *et al.*, 1997; Lukatela *et al.*, 1998), may support the thesis that both enzyme subclasses developed evolutionarily from a common ancestor. The activity of these hydrolases can be measured as a function of the release of free *p*-nitrophenol from the sulfate ester (Sinchaikul *et al.*, 2002; Liu *et al.*, 2000). In the case of sulfotransferase assays, the role of pNPS is rather to be a part of the PAPS regenerating system (PAPS is 3′-phosphoadenosine-5′-phosphosulfate; Chou *et al.*, 1998; Frame *et al.*, 2000). Sulfatases are enzymes involved in a huge number of biochemical processes and their physiological importance can be illustrated by the numerous disorders to which they are linked (Mehl & Jatzkewitz, 1964; Coughtrie *et al.*, 1998; Parenti *et al.*, 1997). Therefore, there have also been a significant number of papers devoted to the substrates of these enzymes, including various nitrophenyl esters (Jones *et al.*, 1984*a*,*b*; Chapman *et al.*, 2003). However, despite the importance of pNPS as a frequently used enzyme substrate, its crystal structure has remained unknown to date. Therefore, we undertook the present X-ray study of the title compound, (I), the potassium salt of pNPS, in order to acquire accurate and reliable data which can be used in molecular modelling enzyme–substrate interaction calculations.



(I)

The molecular structure of the pNPS anion of (I) is shown in Fig. 1. A slight deviation from the coplanarity of the nitro group in relation to the plane of the aryl ring is observed, with an interplanar angle of 12.1 (3)°. The orientation of the sulfate group in relation to the benzene ring is found to be −*sc*; the S—O1—C1—C2 torsion angle is −79.0 (2)°. The S—O1 ester bond length is 1.631 (2) Å, which corresponds well with the average value found for other aromatic sulfate esters (Popek, 1998). The values of the remaining S—O bond lengths are between 1.439 (2) and 1.442 (2) Å, which also correspond with those observed in other aromatic sulfate esters. Deformation from the ideal tetrahedral shape around the S atom is observed: the valence angles at the S atom range from 99.91 (9) to 115.66 (10)° (for O1—S—O2 and O2—S—O3, respectively). Conjugation between the π-system of the aromatic ring and the strongly electron-withdrawing nitro group in the *para* position contributes to the significant shortening of the O1—C1 bond; the value of 1.390 (2) Å is the shortest among all known structures of sulfate monoesters (Popek, 1998). Selected geometric parameters for the anion in (I) are given in Table 1.

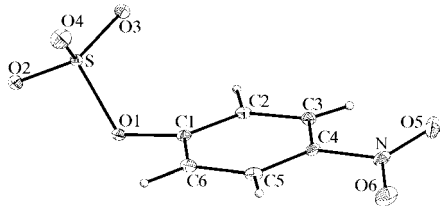


Figure 1
The molecular structure of the *p*-nitrophenyl sulfate anion of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

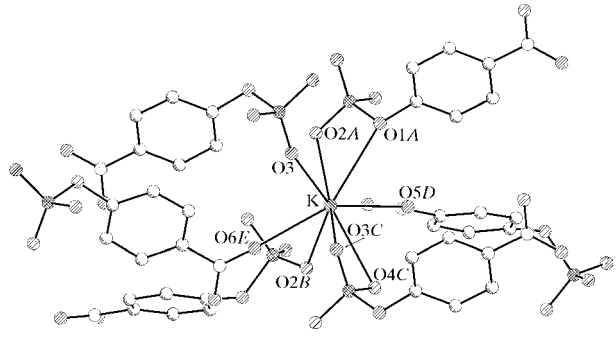


Figure 2
The coordination sphere of the K^+ ion of (I). H atoms have been omitted for clarity. Symmetry codes: (*A*) $1-x, 1-y, 1-z$; (*B*) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (*C*) $2-x, 1-y, 1-z$; (*D*) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (*E*) $\frac{1}{2}+x, y, \frac{3}{2}-z$.]

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The coordination sphere of the K^+ ion may be described as a distorted square antiprism composed of eight O atoms (Fig. 2), *viz*. six O atoms from four sulfate groups and two O atoms from two nitro groups. The K—O distances of the coordination sphere are given in Table 1.

The structure of the *p*-nitrophenyl sulfate anion of (I) is stabilized by short C—H···O intermolecular contacts and π–π stacking interactions. Two anions are linked by C—H···O contacts to form a centrosymmetrical head-to-head dimer [$R_2^2(12)$ ring], as shown in Fig. 3. Each dimer is linked to one other *via* two C—H···O contacts, namely C2—H2···O4($\frac{3}{2}-x$, $y-\frac{1}{2}$, z) and C3—H3···O4($\frac{3}{2}-x$, $y-\frac{1}{2}$, z), with a bifurcated O4 acceptor (Fig. 4 and Table 2). Fig. 5 shows the π–π stacking interactions, which create a zigzag line along the *a* axis. The interplanar spacing between the centroids of parallel benzene rings is 3.58 (1) Å.

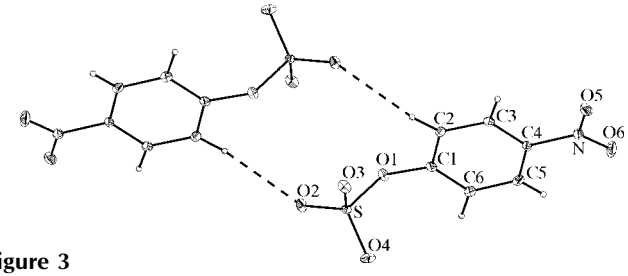

Figure 3
A view of the crystal packing of (I), showing the centrosymmetric $R_2^2(12)$ dimer formed by two anions placed head-to-head. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

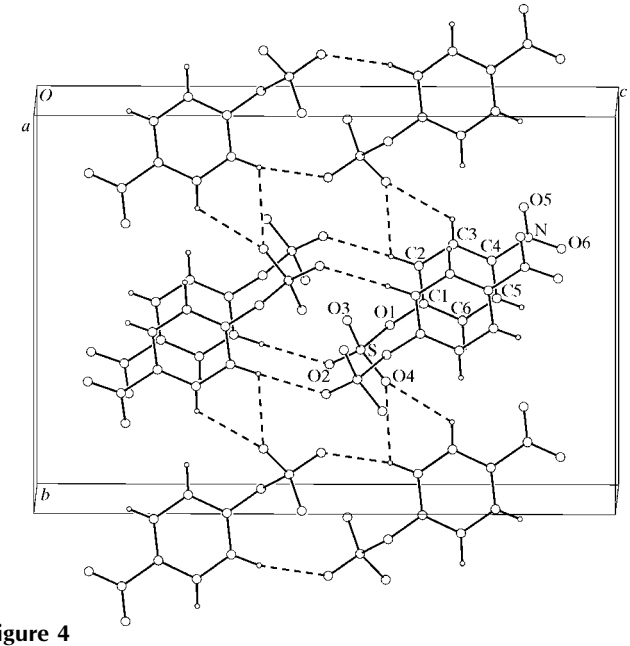

Figure 4
A packing diagram for (I), with the inter- and intradimeric C—H···O interactions shown as dashed lines.

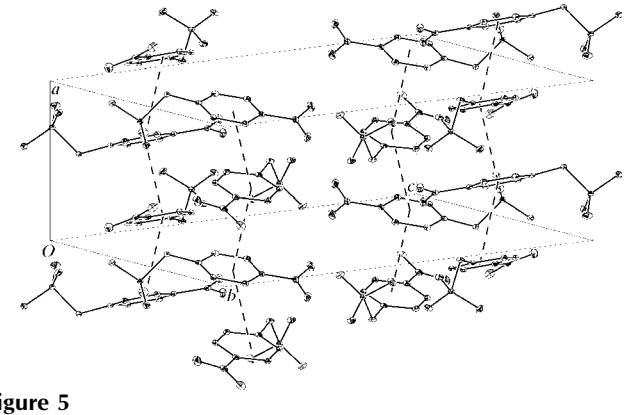

Figure 5
A diagram showing the π–π stacking interactions in (I), marked as dashed lines, to illustrate the zigzags. The K^+ ions and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

Colourless acicular crystals of potassium *p*-nitrophenyl sulfate were obtained by slow evaporation of a water solution of the commercial compound (obtained from Fluka Co.) at room temperature.

Crystal data

$K^+\cdot C_6H_4NO_6S^-$
$M_r = 257.26$
Orthorhombic, *Pbca*
$a = 6.905$ (3) Å
$b = 13.116$ (5) Å
$c = 18.969$ (11) Å
$V = 1717.9$ (14) Å^3
$Z = 8$
$D_x = 1.989$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 66 reflections
$\theta = 2.2$–$30.0°$
$\mu = 0.87$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.50 × 0.10 × 0.08 mm

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
12 140 measured reflections
2514 independent reflections
1779 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 30.0°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -26 \rightarrow 26$
3 standard reflections
every 100 reflections
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

K—O3	2.678 (2)	S—O4	1.442 (2)
K—O1^{i}	3.024 (2)	S—O2	1.442 (2)
K—O2^{i}	2.773 (2)	S—O1	1.631 (2)
K—O2^{ii}	2.751 (2)	O1—C1	1.390 (2)
K—O3^{iii}	2.958 (2)	C4—C5	1.389 (3)
K—O4^{iii}	3.041 (2)	C4—N	1.463 (3)
K—O5^{iv}	2.903 (2)	N—O6	1.225 (3)
K—O6^{v}	2.897 (2)	N—O5	1.234 (3)
S—O3	1.439 (2)		
C1—O1—S	118.9 (2)	C5—C4—N	118.7 (2)
C2—C1—O1	120.0 (2)	O6—N—O5	123.7 (2)
O1—C1—C6	118.0 (2)	O6—N—C4	118.1 (2)
C3—C4—N	118.9 (2)	O5—N—C4	118.2 (2)
O3—S—O1—C1	56.4 (2)	C3—C4—N—O6	−167.8 (2)
O4—S—O1—C1	−63.6 (2)	C5—C4—N—O6	10.9 (3)
O2—S—O1—C1	177.1 (2)	C3—C4—N—O5	12.1 (3)
S—O1—C1—C2	−79.0 (2)	C5—C4—N—O5	−169.2 (2)
S—O1—C1—C6	106.5 (2)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (iii) $2-x, 1-y, 1-z$; (iv) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $\frac{1}{2}+x, y, \frac{3}{2}-z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.329P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.085$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.43$ e Å^{-3}
2514 reflections	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
153 parameters	Extinction coefficient: 0.0014 (5)
All H-atom parameters refined	

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2^{i}	0.98 (3)	2.57 (3)	3.401 (3)	143 (2)
C2—H2···O4^{ii}	0.98 (3)	2.69 (3)	3.225 (3)	115 (2)
C3—H3···O4^{ii}	0.90 (3)	2.55 (3)	3.133 (3)	123 (2)
C6—H6···O5^{vi}	1.00 (3)	2.63 (3)	3.442 (3)	138 (2)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (vi) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

All H atoms were found in difference Fourier maps and were refined isotropically [C—H = 0.87 (3)–1.00 (3) Å].

Data collection: *KM*-4 *User's Guide* (Kuma, 1989); cell refinement: *KM*-4 *User's Guide*; data reduction: *KM*-4 *User's Guide*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1726). Services for accessing these data are described at the back of the journal.

References

Bond, C. S., Clements, P. R., Ashby, S. J., Collyer, C. A., Harrop, S. J., Hopwood, J. J. & Guss, J. M. (1997). *Structure*, **5**, 277–289.

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Chapman, E., Bryan, M. C. & Wong, C.-H. (2003). *Proc. Natl Acad. Sci.* **100**, 910–915.

Chou, H.-C., Ozawa, S., Fu, P. P., Lang, N. P. & Kadlubar, F. F. (1998). *Carcinogenesis*, **19**, 1071–1076.

Coughtrie, M. W. H., Sharp, S., Maxwell, K. & Innes, N. P. (1998). *Chem. Biol. Interact.* **109**, 3–27.

Dodgson, K. S., Spencer, B. & Williams, K. (1956). *Biochem. J.* **64**, 216–221.

Frame, L. T., Ozawa, S., Nowell, S. A., Chou, H.-C., DeLongchamp, R. R., Doerge, D. R., Lang, N. P. & Kadlubar, F. F. (2000). *Drug Metab. Dispos.* **28**, 1063–1068.

Jones, P. G., Sheldrick, G. M., Kirby, A. J. & Abell, K. W. Y. (1984*a*). *Acta Cryst.* C**40**, 547–549.

Jones, P. G., Sheldrick, G. M., Kirby, A. J. & Abell, K. W. Y. (1984*b*). *Acta Cryst.* C**40**, 550–552.

Kuma (1999). *KM*-4 *User's Guide*. Kuma Diffraction, Wrocław, Poland.

Liu, J.-W., Verger, D., Carr, P. D., Yang, H. & Ollis, D. L. (2000). *Acta Cryst.* D**56**, 900–901.

Lukatela, G., Krauss, N., Theis, K., Selmer, T., Gieselmann, V., von Figura, K. & Saenger, W. (1998). *Biochemistry*, **37**, 3654–3664.

Mehl, E. & Jatzkewitz, H. (1964). *Hoppe-Seyler's Z. Physiol. Chem.* **339**, 260–276.

O'Brien, P. J. & Herschlag, D. (2001). *Biochemistry*, **40**, 5691–5699.

Parenti, G., Meroni, G. & Ballabio, A. (1997). *Curr. Opin. Genet. Dev.* **7**, 386–391.

Popek, T. (1998). PhD thesis, Faculty of Chemistry, University of Wrocław, Poland.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sinchaikul, S., Tyndall, J. D. A., Fothergill-Gilmore, L. A., Taylor, P., Phutrakul, S., Chen, S.-T. & Walkinshaw, M. D. (2002). *Acta Cryst.* D**58**, 182–185.

Suiko, M., Tojo, T., Fernando, P. H. P., Sakakibara, Y., Kawano, J. & Liu, M. C. (1996). *Biosci. Biotechnol. Biochem.* **60**, 137–138.