

Sodium *p*-nitrophenolate tetrahydrateS. Brahadeeswaran,^{a†} H. L. Bhat,^a J. N. Sherwood^b and R. M. Vrcelj^{c*}^aDepartment of Physics, Indian Institute of Science, Bangalore 560 012, India, ^bDepartment of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, and ^cCombinatorial Centre of Excellence, Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England

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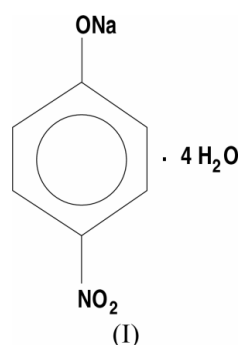
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Key indicators

Single-crystal X-ray study
T = 123 K
Mean $\sigma(C-C)$ = 0.003 Å
R factor = 0.041
wR factor = 0.101
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The structure of sodium *p*-nitrophenolate tetrahydrate, Na⁺·C₆H₄NO₃⁻·4H₂O, is presented. The nature of the hydrogen and coordination bonds in this structure is discussed and compared with that of sodium *p*-nitrophenolate dihydrate.Received 12 April 2002
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Comment

The influence of solvents on crystallization in the formation of new structures of organic compounds is well known and this effect can pose serious problems when crystallizing materials for non-linear optical (NLO) applications. Minemoto *et al.* (1994) have reported problems associated with the selection of solvents for growing crystals of sodium *p*-nitrophenolate dihydrate (NPNa·2H₂O), a recent NLO material. This orthorhombic dihydrate system (Minemoto *et al.*, 1992) was formed when crystallized from methanol solution, whereas the water solvent gave transparent crystals in solution, but these lost their transparency on exposure to air. We have carried out further investigations on the growth of NPNa with water as solvent. During the course of this study, we found two types of crystals, *viz.* monoclinic tetrahydrate and monoclinic monohydrate, which are easily distinguishable by their colour, the former being yellow and the latter being red-brown. Some mention of the tetrahydrate form has already been made in a previous report (Brahadeeswaran *et al.*, 1998). The present study reports the structure of this tetrahydrate form, (I), in more detail.



In the tetrahydrate form, we have observed extensive hydrogen bonding. Both O1A and O1B of the nitrophenoxy ions in the asymmetric unit shown in Fig. 1 are hydrogen bonded to four O atoms of the solvate water molecules. The O atoms of the NO₂ group also form hydrogen bonds with water molecules (Table 1). The availability of relatively more water molecules, as well as Na⁺ ions in special positions in this form (see Fig. 2), alters the hydrogen-bonding patterns, compared to the well studied dihydrate form, in which the water molecule is hydrogen bonded only to atom O1 of the nitro-

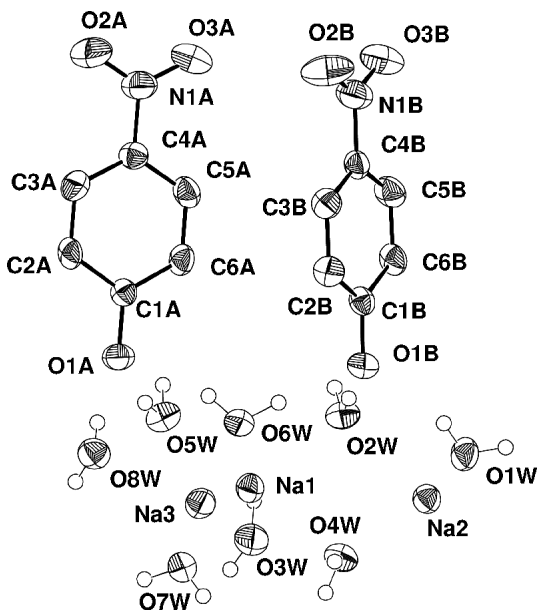


Figure 1
The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids. [Please provide revised figure with labels shifted off the ellipsoids.]

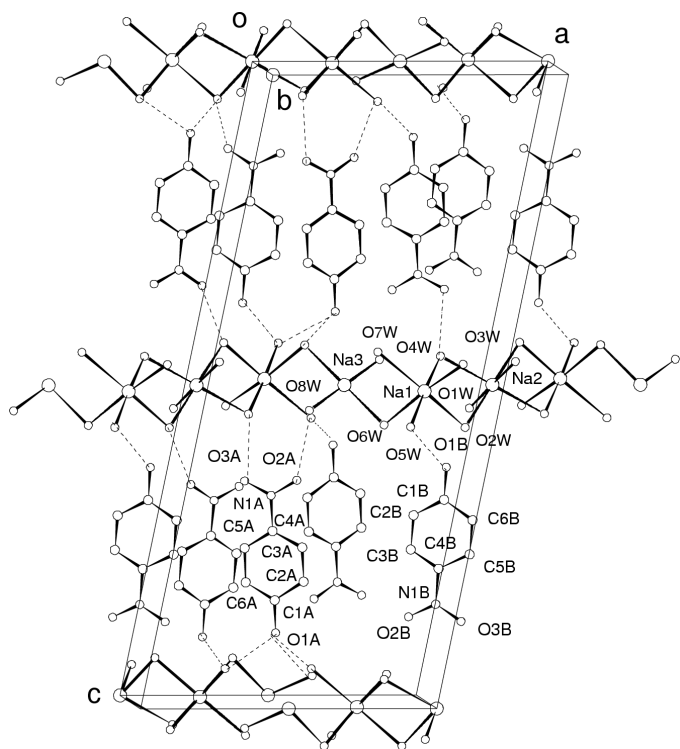


Figure 2
Packing diagram of the crystal structure of the title compound.

phenolate (Minemoto *et al.*, 1992). While the Na atom in the tetrahydrate structure forms regular coordination bonds with six neighbouring OW atoms, resulting in octahedral stacking along the crystallographic *a* axis, the Na⁺ cation in the dihy-

drate form interacts only with atom O2 of the NO₂ group and atoms O3 and OW.

Experimental

The title compound was synthesized from equimolar solutions of *p*-nitrophenolate and sodium hydroxide in water. Single crystals of the tetrahydrate form were grown from aqueous solution by solvent evaporation at 300 K. These crystals were found to nucleate and grow to suitable size for examination after 1 d of solution preparation.

Crystal data

Na⁺·C₆H₄NO₃⁻·4H₂O
M_r = 233.16
 Monoclinic, *P*2₁/*c*
a = 11.844 (2) Å
b = 6.8736 (12) Å
c = 25.939 (6) Å
 β = 101.038 (17)°
V = 2072.6 (7) Å³
Z = 8
D_x = 1.49 Mg m⁻³
D_m = 1.44 Mg m⁻³

D_m measured by flotation in CHBr₃/
 C₆H₅CH₃
 Mo *K*α radiation
 Cell parameters from 25
 reflections
 θ = 12.0–15.1°
 μ = 0.17 mm⁻¹
T = 123 (2) K
 Block, yellow
 0.3 × 0.2 × 0.2 mm

Data collection

Rigaku AFC-7S four-circle
 diffractometer
 ω scans
 5184 measured reflections
 4641 independent reflections
 4267 reflections with *I* > 2σ(*I*)
R_{int} = 0.016

θ_{\max} = 27.5°
h = 0 → 15
k = 0 → 8
l = -33 → 31
 3 standard reflections
 every 150 reflections
 intensity decay: 4.0%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.041
wR(*F*²) = 0.101
S = 1.12
 4641 reflections
 370 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 2.0621P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3W—H9···O1A ⁱ	0.84 (3)	2.00 (3)	2.828 (2)	166 (3)
O3W—H10···O1B ⁱ	0.85 (3)	1.93 (3)	2.765 (2)	168 (2)
O5W—H11···O8W	0.86 (3)	1.92 (3)	2.769 (2)	170 (3)
O5W—H12···O3A ⁱⁱ	0.80 (3)	2.12 (3)	2.916 (2)	171 (3)
O7W—H13···O1B ⁱ	0.82 (3)	1.97 (3)	2.781 (2)	167 (2)
O1W—H14···O6W	0.86 (3)	1.93 (3)	2.763 (2)	164 (2)
O6W—H15···O2B ⁱⁱⁱ	0.86 (3)	2.11 (3)	2.924 (2)	158 (3)
O2W—H16···O1A ⁱⁱⁱ	0.86 (3)	2.00 (3)	2.857 (2)	176 (3)
O7W—H17···O3B ^{iv}	0.85 (3)	2.05 (3)	2.891 (2)	170 (2)
O6W—H18···O1W ^v	0.83 (3)	1.96 (3)	2.778 (2)	166 (3)
O1W—H19···O1B ^{vi}	0.81 (3)	2.01 (3)	2.753 (2)	153 (3)
O2W—H20···O2A ⁱⁱ	0.82 (3)	2.10 (3)	2.908 (2)	170 (3)
O8W—H21···O1A	0.79 (3)	2.01 (3)	2.781 (2)	164 (3)
O8W—H22···O4W ^{vii}	0.81 (3)	1.99 (3)	2.791 (2)	171 (3)
O4W—H23···O1A ⁱ	0.91 (3)	1.85 (3)	2.744 (2)	171 (2)
O4W—H24···O1B ^{viii}	0.83 (3)	2.04 (3)	2.856 (2)	168 (3)

Symmetry codes: (i) 1 - *x*, 2 - *y*, - *z*; (ii) 1 - *x*, *y* - ½, ½ - *z*; (iii) *x*, *y* - 1, *z*; (iv) *x* - 1, ½ - *y*, *z* - ½; (v) - *x*, 1 - *y*, - *z*; (vi) *x* - 1, *y*, *z*; (vii) *x*, 1 + *y*, *z*; (viii) 1 - *x*, 1 - *y*, - *z*.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *INSIGHTII* (Biosym Technologies, 1995) and *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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