Sodium 4-(2-pyridinyldiazenyl)-resorcinolate monohydrate and ammonium 2,4-dinitro-1-naphthalenolate from powder diffraction data

A. V. Yatsenko,[a]* K. A. Paseshnichenko,[a] V. V. Chernyshev[a] and H. Schenk[b]

[a]Chemistry Department, Moscow State University, 119899 Moscow, Russia, and [b]Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, 1018 WV, The Netherlands

Correspondence e-mail: yatsenko@biocryst.phys.msu.su

The crystal structures of two dyestuffs, $Na^+ \cdot C_{11}H_8N_3O_2^- \cdot H_2O$, (I), and $NH_4^+ \cdot C_{10}H_5N_2O_5^-$, (II), were determined from X-ray powder diffraction data. In both structures, translationally related anions form stacks, and cations fill interstack channels. A comparison of the diffuse reflectance spectra of crystalline (I) and (II) with the absorption spectra of their aqueous solutions demonstrates that the geometry of their anions does not change significantly upon transfer from the crystalline to the solution state.

Comment

Both compounds studied are widely used colorants: (I) is a metallochromic indicator (the acronym PAR is used for the neutral molecule, as well as for its sodium salts) and (II) is an anionic dye (Acid Yellow 24). PAR is known to exist in aqueous solution at pH 6.0–11.0 predominantly as the monoanion, with a deprotonated *para*-OH group with respect to the azo linkage (Geary *et al.*, 1962). Deprotonation of the *ortho*-OH group occurs only at pH > 11.0, because this OH group is involved in a strong intramolecular hydrogen bond with the azo-N atom farthest from the resorcinol ring (Shibata, 1972). Although the level of precision of this study is not enough to locate H atoms, the N2 and O3 atoms have a close contact [O3···N2 2.52 (1) Å], so that they appear to be involved in an intramolecular hydrogen bond, whereas for the *o*-deprotonated anion, the turn through 180° about the C4—N1 bond is expected. Surprisingly, neither *AM*1 nor *PM*3 calculations are able to predict properly the relative stability of *p*- and *o*-deprotonated species; they predict that the *ortho* form is more stable by 5.1 and 1.6 kJ mol^{-1}, respectively. This may be a consequence of the fact that both these methods underestimate a contribution of the intramolecular hydrogen bonds to the stabilization of the corresponding tautomer (Rios & Rodriguez, 1992), although *PM*3 is generally superior to

*AM*1 in reproducing hydrogen-bond geometry (Jurema & Schields, 1993).

(I)   (II)
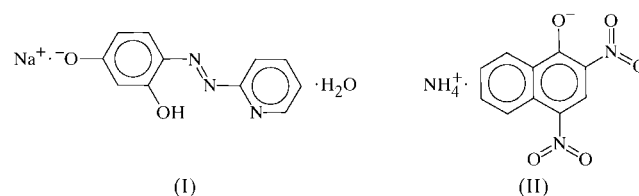
The anion in (I) is slightly non-planar and the pyridine ring is twisted by 10.9 (4)° with respect to the resorcinol ring. The anions form stacks along [010] with interplanar distances of 3.31 (1) and 3.40 (1) Å for the resorcinol and pyridine rings, respectively (Fig. 1). The Na$^+$ cation is surrounded by five O atoms (two water molecules, one *ortho*- and two *para*-O atoms, Table 1), which form a distorted tetragonal pyramid. The water molecule makes contacts to two Na$^+$ cations and as a hydrogen donor forms a strong hydrogen bond to the O1 atom and a medium–strong bond to the N8 atom. The angles at the O2 atom are close to tetrahedral values.

The positions of the maxima in the diffuse reflection spectrum of crystalline (I) (403 nm) and in the absorption spectrum of its aqueous solution (414 nm; Molina *et al.*, 1999)
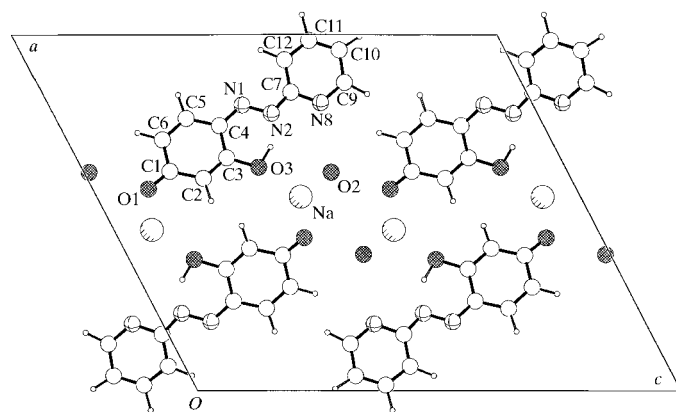

Figure 1
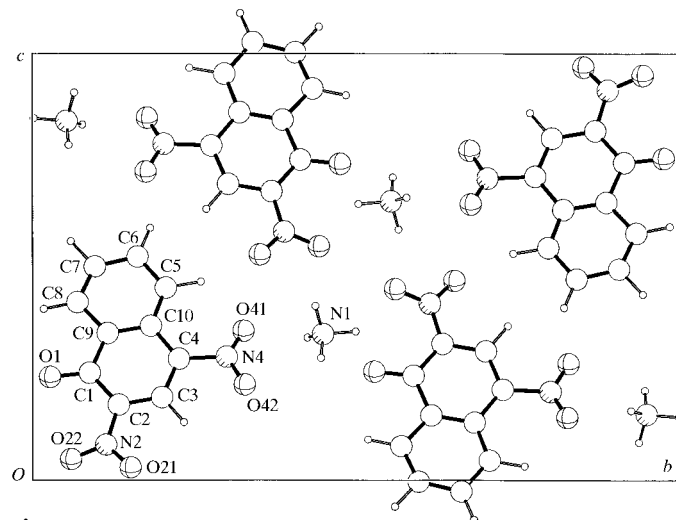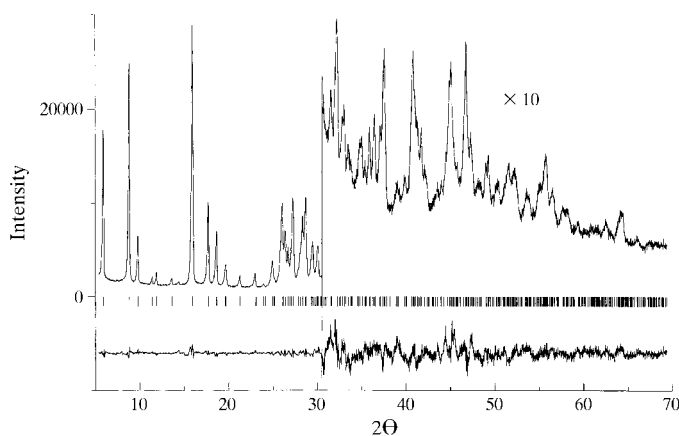Packing diagram of (I) viewed along [010].

Figure 2
Packing diagram of (II) viewed along [100].

Figure 3
The Rietveld plot for (I) showing the observed and difference profiles. The reflection positions are shown above the difference profile.

coincide closely, thus no significant distinctions between the structures of the monoanion in the solid state and in solution could be expected, except for the twist of the pyridine ring in solution to minimize the steric crowding. Because the barrier to rotation about the N2—C7 bond appears to be low, the pyridyl group is free to rotate in solution. However, according to INDO/S calculations, the effect of the pyridine twisting on the position of the absorption maximum is not large, *ca* 900 cm^{-1}, thus it can be overshadowed by other effects, such as intermolecular hydrogen bonding. The twist of the pyridine ring in the solvated monoanion is in line with the finding that in the first stage of complex formation, PAR coordinates to the metal ion *via* the pyridine N atom, and in the second stage (slow), a bond to the azo-N atom forms (Shi *et al.*, 1998).

As a result of sterical tensions, the *para*- and *ortho*-nitro groups in the 2,4-dinitro-1-naphthalenolate anion (Fig. 2) are twisted out of the plane of the naphthalene bicycle by 14.6 (4) and 20.1 (4)°, respectively. The *PM*3-calculated twist angles are very similar: 9.0 and 19.8°, respectively. The ammonium cation is surrounded by eight O atoms (N1···O < 3.5 Å, Table 2), which form an irregular polyhedron with a shortest O···O distance of 3.03 (1) Å. The cation is displaced by 0.6 Å from the centre of this polyhedron towards two naphthalenolate O1
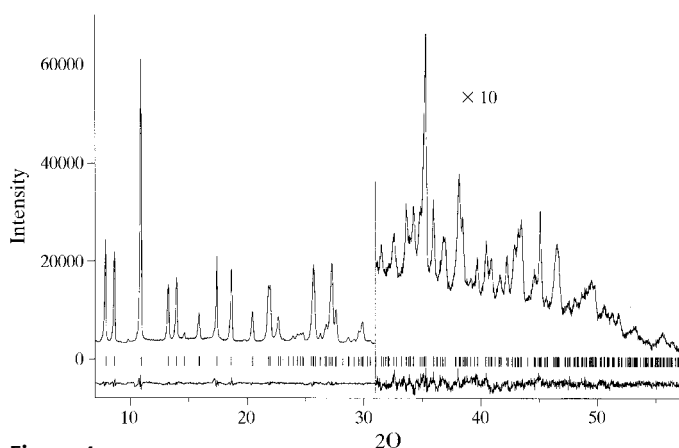
Figure 4
The Rietveld plot for (II) showing the observed and difference profiles. The reflection positions are shown above the difference profile.

atoms. The interplanar distance between naphthalene bicycles within the stack is 3.55 (1) Å.

The diffuse reflectance spectrum of crystalline (II) contains two well resolved absorption maxima (λ_{max} = 447 and 394 nm), which also appear in the spectrum of its aqueous solution (λ_{max} = 439 and 394 nm; Hamann & Linton, 1974; Bordwell *et al.*, 1980). INDO/S calculations give two long-wavelength π–π^* transitions for this anion, and the separation between them decreases upon the twist of the nitro groups out of the naphthalene plane. As this separation is slightly larger in the spectrum of crystalline (II) than in the spectrum of its solution (53 *versus* 45 nm, respectively), it may be supposed that the anion of (II) flattens upon transfer from aqueous solution to the crystalline state.

Experimental

Commercially obtained preparates were recrystallized from aqueous solutions. The UV–visible spectra were recorded on a Specord M-40 spectrophotometer (Carl Zeiss, Jena).

Compound (I)

Crystal data

Na$^+$·C$_{11}$H$_8$N$_3$O$_2^-$·H$_2$O	Cu $K\alpha$ radiation
M_r = 255.21	Cell parameters from 56
Monoclinic, $P2_1/c$	reflections
a = 16.703 (3) Å	θ = 3.0–32.1°
b = 3.634 (1) Å	μ = 1.31 mm^{-1}
c = 20.248 (3) Å	T = 295 (2) K
β = 117.38 (1)°	Specimen shape: flat sheet
V = 1091.4 (5) Å^3	25 × 25 × 2.0 mm
Z = 4	Plate, orange
D_x = 1.553 Mg m^{-3}	

Data collection

DRON-3M diffractometer (Bure-	h = 0 → 12
vestnik, Russia)	k = 0 → 2
Specimen mounting: pressed as a	l = −15 → 15
thin layer in the specimen holder	$2\theta_{min}$ = 5.4, $2\theta_{max}$ = 70.0°
Specimen mounted in reflection	Increment in 2θ = 0.02°
mode	

Refinement

R_p = 0.038	H-atom parameters not refined
R_{wp} = 0.050	Weighting scheme based on
R_{exp} = 0.023	measured s.u.'s
S = 2.14	$(\Delta/\sigma)_{max}$ = 0.045
$2\theta_{min}$ = 5.4, $2\theta_{max}$ = 69.4°	$\Delta\rho_{max}$ = 0.6 e Å^{-3}
Increment in 2θ = 0.02°	$\Delta\rho_{min}$ = −0.8 e Å^{-3}
Excluded region(s): 69.42–70.00	Preferred orientation correction:
Profile function: split-type pseudo–	March–Dollase (Dollase, 1986)
Voigt	along [010], G$_1$ = 0.865 (1)
104 parameters	

Table 1
Selected geometric parameters (Å, °) for (I).

Na—O2	2.561 (13)	Na—O1^{iii}	2.590 (12)
Na—O3	2.231 (11)	O2—N8	2.942 (15)
Na—O2^i	2.328 (13)	O2—O1^{iv}	2.596 (14)
Na—O1^{ii}	2.411 (11)		
Na—O2—N8	114 (1)	N8—O2—Na^v	106 (1)
Na—O2—Na^v	96 (8)	N8—O2—O1^{iv}	115 (1)
Na—O2—O1^{iv}	105 (1)	Na^v—O2—O1^{iv}	120 (1)

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

Compound (II)

Crystal data

$NH_4^+ \cdot C_{10}H_5N_2O_5^-$
$M_r = 251.20$
Monoclinic, $P2_1/c$
$a = 3.924 (1)$ Å
$b = 20.314 (4)$ Å
$c = 13.336 (3)$ Å
$\beta = 94.31 (1)°$
$V = 1060 (1)$ Å^3
$Z = 4$
$D_x = 1.574$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 48 reflections
$\theta = 3.9–22.6°$
$\mu = 1.11$ mm^{-1}
$T = 295 (2)$ K
Specimen shape: flat sheet
$25 \times 25 \times 2.0$ mm
Plate, orange–red

Data collection

DRON-3M diffractometer (Burevestnik, Russia)
Specimen mounting: pressed as a thin layer in the specimen holder
Specimen mounted in reflection mode

$h = 0 \rightarrow 2$
$k = 0 \rightarrow 13$
$l = -8 \rightarrow 8$
$2\theta_{min} = 5.5$, $2\theta_{max} = 60.0°$
Increment in $2\theta = 0.02°$

Refinement

$R_p = 0.023$
$R_{wp} = 0.030$
$R_{exp} = 0.015$
$S = 2.01$
$2\theta_{min} = 7.0$, $2\theta_{max} = 57.0°$
Increment in $2\theta = 0.02°$
Profile function: split-type pseudo–Voigt
106 parameters

H-atom parameters not refined
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max} = 0.04$
$\Delta\rho_{max} = 0.8$ e Å^{-3}
$\Delta\rho_{min} = -0.7$ e Å^{-3}
Preferred orientation correction: March–Dollase (Dollase, 1986) along [100], $G_1 = 1.338 (1)$

Table 2
Selected bond lengths (Å) for (II).

N1—O41	3.43 (1)	N1—O22^{ii}	2.96 (1)
N1—O42	3.07 (1)	N1—O41^{iii}	2.96 (1)
N1—O1^i	2.77 (1)	N1—O22^{iv}	3.06 (1)
N1—O1^{ii}	2.81 (1)	N1—O21^{iv}	3.21 (1)

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

The monoclinic cell dimensions of (I) and (II) were determined with *TREOR*90 (Werner *et al.*, 1985) and refined to $M_{20} = 29$ and 40, and $F_{30} = 37(0.011,76)$ and $72(0.007,60)$ using the first 56 and 48 peak positions, respectively. The positions of the cations and anions were determined using the grid-search procedure (Chernyshev & Schenk, 1998). The initial anion models were built with *MOPAC*7 (Stewart, 1993) on the *PM*3 level (Stewart, 1989), the solvent effect being taken into account using the *COSMO* approach (Klamt & Schüürmann, 1993). The X-ray diffraction profile and the difference between the measured and calculated profiles after the Rietveld refinement are shown in Figs. 3 and 4; final $R_B = 0.077$ and 0.072. All atoms were refined isotropically and were gathered together into groups with a common U_{iso} parameter for each group. H atoms were placed in geometrically calculated positions and their isotropic displacement parameters were fixed. The NH_4^+ cation in the structure of (II) was allowed to rotate as a rigid tetrahedron. In (I), no H atoms were included for the water molecule. The planarity of the pyridine and resorcinol rings in (I) and of the naphthalene fragment and nitro groups in (II) was restrained. The anisotropy of diffraction-line broadening was approximated by a quartic form in *hkl* (Popa, 1998). The standard uncertainties obtained from the Rietveld refinement were corrected for serial correlation effects (Bérar & Lelann, 1991). INDO/S calculations were carried out with the *INDO–CISD* program (Dick & Nickel, 1983).

For both compounds, data collection: local program; cell refinement: *LSPAID* (Visser, 1986); program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLUTON* (Spek, 1992); software used to prepare material for publication: *PARST* (Nardelli, 1983).

References

Bérar, J.-F. & Lelann, P. (1991). *J. Appl. Cryst.* **24**, 1–5.
Bordwell, F. G., Branca, J. C., Hughes, D. L. & Olmstead, W. N. (1980). *J. Org. Chem.* **45**, 3305–3313.
Chernyshev, V. V. & Schenk, H. (1998). *Z. Kristallogr.* **213**, 1–3.
Dick, B. & Nickel, B. (1983). *Chem. Phys.* **1**, 1–16.
Dollase, W. A. (1986). *J. Appl. Cryst.* **19**, 267–272.
Geary, W. J., Nickless, G. & Pollard, F. H. (1962). *Anal. Chim. Acta*, **26**, 575–582.
Hamann, S. D. & Linton, M. (1974). *J. Chem. Soc. Faraday Trans.* 1, **70**, 2239–2249.
Jurema, M. W. & Shields, G. C. (1993). *J. Comput. Chem.* **14**, 89–109.
Klamt, A. & Schüürmann, G. (1993). *J. Chem. Soc. Perkin Trans.* 2, pp. 799–805.
Molina, M. F., Bosque-Sendra, J. M., Nechar, M. & El Bergmi, R. (1999). *Anal. Chim. Acta*, **389**, 281–290.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Popa, N. C. (1998). *J. Appl. Cryst.* **31**, 176–180.
Rios, M. A. & Rodriguez, J. (1992). *J. Comput. Chem.* **13**, 860–866.
Shi, Y., Eyring, E. M. & van Eldik, R. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3565–3576.
Shibata, Sh. (1972). *Chelates in Analytical Chemistry*, Vol. 4, edited by H. A. Flaschka & A. J. Barnard, pp. 1–224. New York: Marcel Dekker.
Spek, A. L. (1992). *PLUTON*92. University of Utrecht, The Netherlands.
Stewart, J. J. P. (1989). *J. Comput. Chem.* **10**, 209–220.
Stewart, J. J. P. (1993). *MOPAC* 7.0. QCPE Program No. 455. Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN, USA.
Visser, J. W. (1986). *Powder Diffr.* **1**, 66–76.
Werner, P.-E., Eriksson, L. & Westdahl, M. (1985). *J. Appl. Cryst.* **18**, 367–370.
Zlokazov, V. B. & Chernyshev, V. V. (1992). *J. Appl. Cryst.* **25**, 447–451.