Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Tetramethylammonium 2,5-dinitrophenolate monohydrate

Genivaldo Julio Perpétuo[a] and Jan Janczak[b]*

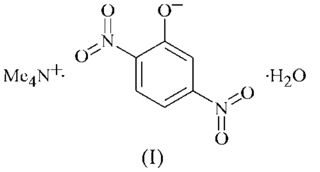
[a]Departamento de Fisica, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, CEP 35.400-000, Ouro Preto, MG, Brazil, and [b]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland
Correspondence e-mail: janczak@int.pan.wroc.pl

Received 21 October 2004
Accepted 13 January 2005
Online 19 February 2005

The crystal structure of the title compound, $C_4H_{12}N^+\cdot C_6H_3N_2O_5^-\cdot H_2O$, is built up from tetramethylammonium cations, 2,5-dinitrophenolate anions and water molecules. The nitro groups are almost coplanar with the aryl ring, which exhibits significant distortion from an ideal hexagonal form. The X-ray geometry of the tetramethylammonium cation shows slight distortion from the tetrahedral symmetry predicted by molecular orbital calculations. The O—H···O hydrogen-bonded water and 2,5-dinitrophenolate units are related by an inversion center and form dimers. The 2,5-dinitrophenolate anions, related by an inversion center and translation, are stacked to form a column along the [100] direction.

Comment

The present study is a continuation of our investigations of compounds with hydrogen-bonding systems that are formed by self-assembly of components containing complementary arrays of hydrogen-bonding sites (Perpétuo & Janczak, 2003; Janczak & Perpétuo, 2004; Desiraju, 1990; Krische & Lehn, 2000; Sherington & Taskinen, 2001). To expand the understanding of the solid-state physical-organic chemistry of compounds containing O—H···O hydrogen-bonding systems, we present here the solid-state structure of tetramethylammonium 2,5-dinitrophenolate monohydrate, (I), and compare the results with those predicted for the isolated oppositely charged parts of the crystal structure of (I), *i.e.* the 2,5-dinitrophenolate anion and the tetramethylammonium cation, by density functional theory (DFT) with fully optimized geometry calculations. Molecular orbital calculations at the B3LYP/6-31+G(*d*) level (Frisch *et al.* 1998) were carried out on isolated ions corresponding to the gas phase.



(I)

The X-ray structure analysis (Fig. 1) reveals that the nitro groups (NO_2) are almost coplanar with the aryl ring [the dihedral angles between the aryl ring and nitro groups are 1.1 (1) and 3.6 (1)°, respectively, for the nitro groups containing atoms N1 and N2]. The aryl ring exhibits distortion from the ideal hexagonal form expected for an unsubstituted benzene ring (see Table 1).

Ionization of the O atom of the hydroxy group influences the C—C bond distances within the aryl ring. The C1—O1 bond length [1.2677 (13) Å] of the ionized hydroxy group shows significant double-bond character, with a value that is intermediate between the values expected for carbon–oxygen double (1.206–1.215 Å) and single (1.333–1.373 Å) bonds, and is closer to the distances of 1.211–1.231 Å found in several benzoquinone derivatives (Allen *et al.*, 1987). The C1—O1 bond is shorter than the equivalent C—O bonds in non-ionized dinitrophenol isomers, for example, 1.331 (7) Å in 2,4-dinitrophenol (Kagawa *et al.*, 1976), 1.337 (7) Å in 2,6-dinitrophenol (Iwasaki *et al.*, 1976) and 1.337 Å in 2,5-dinitrophenol (the value obtained from our molecular orbital calculations; see Fig. 2). The double-bond character of the C1—O1 bond increases the single-bond character of both adjoining C—C bonds of the ring (C1—C2 and C1—C6; Table 1). These bonds are significantly longer than the other four in the ring; thus, the delocalization of the π electrons is disturbed by the donating effect of the O atom of the ionized hydroxy group, and the π electrons are not fully delocalized over all C atoms within the ring. Two of the internal C—C—C angles in the ring, at atoms C1 and C4 (*para* to the hydroxy substituent at atom C1), are significantly smaller than 120°, while the other four C—C—C angles are greater than 120°. These distortions also result from the steric effect of the lone pairs of electrons on the O atom of the ionized hydroxy group.

A search of the Cambridge Structural Database (Allen, 2002) for structures containing ionized dinitrophenol derivatives identifies several structures. Most are structures of the 2,4-dinitrophenolate anion, one is of 2,6-dinitrophenolate (Andersen *et al.* 1989), and no structure is reported for the 2,5-dinitrophenlate anion. Thus, the present structure is the first describing the ionized form of 2,5-dinitrophenol.

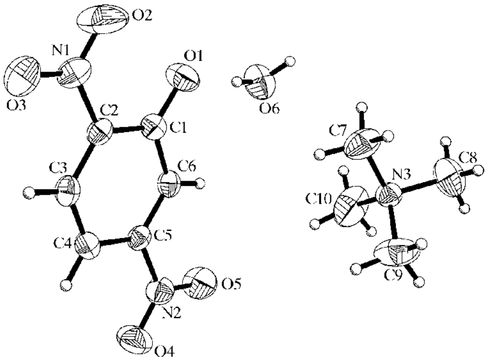


Figure 1
A view of the molecular structure of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii.

DOI: 10.1107/S0108270105001253

The C—NO_2 bonds are short but well within the range [1.445 (7)–1.476 (7) Å] found for aryl groups doubly substituted by nitro groups (Allen, 2002). The O—N—O angles in the NO_2 groups are greater than 120° as a result of the steric effect of lone pairs of electrons on both the O atoms of the NO_2 groups. This effect is predicted by the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992). The distortion of the O—N—O angle from 120° is smaller in the NO_2 group at the position (at C2) *ortho* to the ionized hydroxy group (at C1) than in the nitro group at the *meta* position (at C5). This difference is likely to be due to the interaction of atom O1 with atom O2 of the neighboring nitro group; both O atoms contain lone-pair electrons.

The optimized geometry of the ionized 2,5-dinitrophenolate anion calculated by DFT methods corresponding to the gas-phase structure is close to planar (Fig. 2), and the optimized geometric parameters correlate well with those found in the crystal; however, the calculated C—C bond lengths in the aryl ring are slightly longer than the X-ray values, especially those of the C—C bonds (C1—C2 and C1—C6) that contain the C atom bonded to the ionized hydroxy group (O1). The shortening of the C1—O1 bond and the lengthening of the C1—C2 and C1—C6 bonds in the ionized 2,5-dinitrophenolate residue in relation to the non-ionized molecule (see Fig. 2) is more evident in the gas phase than in the crystal, since in the crystal structure the O atom is involved as an acceptor in hydrogen bonds with water molecules (Table 2). The delocalization of the charge of the ionized hydroxy group along the C1—O1 bond makes the length of this bond closer to that of a double bond. The molecular orbital calculations also demonstrate that ionization of the hydroxy group leads to a decrease in the internal C—C—C angle at the C atom bonded to the O atom of the ionized hydroxy group, from 117.8° (in the non-ionized molecule) to 112.9°. In addition, the C2—C1—O1 angle increases by 2.5°, since in the non-ionized molecule an intramolecular O1—H1···O2 hydrogen bond is present (Fig. 2). From the *ab initio* and X-ray results, we can conclude that the ring distortions in the ionized 2,5-dinitrophenolate moiety result mainly from the ionization of the hydroxy group; the ionization changes the electronic structure as a result of the donating effect of ionized hydroxy group. The charge of the ionized hydroxy group is delocalized in the direction of the benzene ring and, in consequence, disturbs the delocalization of the π electrons in the ring.

The X-ray geometry of the tetramethylammonium cation shows slight distortion from the tetrahedral geometry obtained by the molecular orbital calculations, due to the interaction with oppositely charged 2,5-dinitrophenlate ions in the crystal; the calculated values of the four C—N bonds and six C—N—C angles in the isolated $(CH_3)_4N^+$ ion are equivalent (1.510 Å and 109.47°, respectively). The calculated N—C bonds in the tetramethylammonium cation are longer than those found in the crystal; the shortening is probably due to the interactions present in the crystal. As can be seen from Fig. 1, the displacement ellipsoids for the cation methyl groups are a little large. However, libration analysis of rigid-body motion according to the method of Schomaker & Trueblood (1968) also predicts similar differences between the gas-phase and solid-state C—N bond lengths and C—N—C angles (the differences between the corrected and uncorrected C—N distances in the X-ray structure are smaller than 3σ). Thus, the distortion of the tetramethylammonium cation from tetrahedral symmetry is probably due to interactions with oppo-

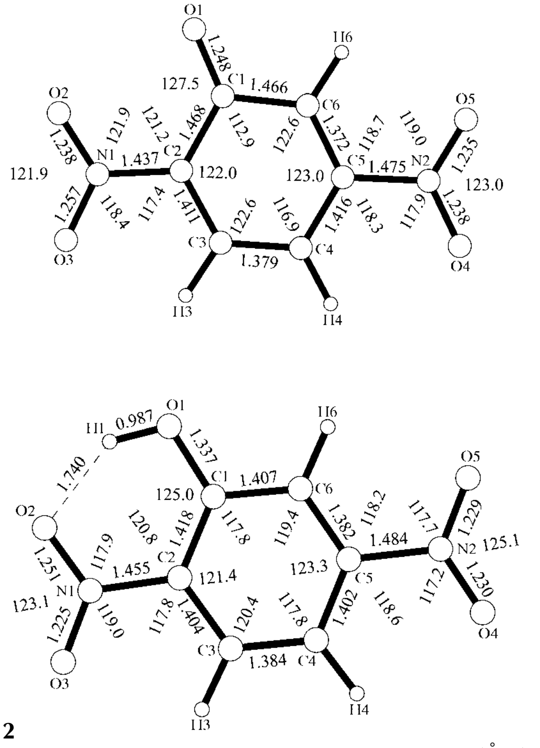


Figure 2

The results of the optimized molecular orbital calculations (Å, °) for the 2,5-dinitrophenolate anion (top) and non-ionized 2,5-dinitrophenol (bottom), illustrating the donating effect of the O atom of the ionized hydroxy group.

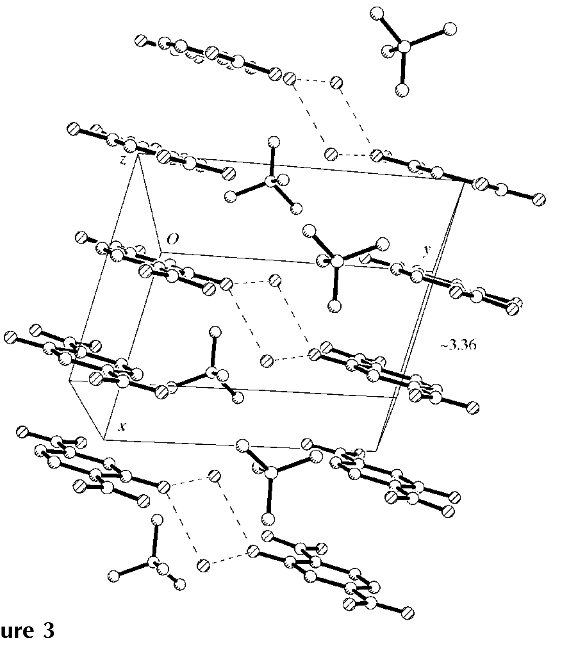


Figure 3

A view of the crystal packing, showing the stacking structure and the O—H···O hydrogen-bonded dimers. H atoms have been omitted for clarity.

sitely charged 2,5-dinitrophenolate moieties. In the crystal packing (Fig. 3), the tetramethylammonium cations are surrounded by 2,5-dinitrophenolate anions that join with the water molecules to form a dimeric structure.

In the crystal structure of (I), 2,5-dinitrophenolate anions related by an inversion center and translation (symmetry code: $1 - x, -y, 1 - z$) are stacked to form a column along the [100] direction (Fig. 3). The aryl rings within the stack are separated by 3.36 (1) Å. This value is consistent with the requirements of π–π stacking interactions and clearly accommodates the 3.4 Å distance required for the overlapping π aromatic ring system (Pauling, 1960); this interaction can contribute to the shortening of the C—C bonds within the ring in relation to the gas-phase structure obtained from molecular orbital calculations. Two water molecules interact *via* O—H···O hydrogen bonds (Table 2) with two 2,5-dinitrophenolate anions related by an inversion center (Table 2) to form a dimeric structure. The tetramethylammonium cations are located in the holes between the O—H···O hydrogen-bonded dimers of water and 2,5-dinitrophenolate moieties, and interact by a combination of van der Waals and ionic interactions with the oppositely charged 2,5-dinitrophenolate anions.

Experimental

Tetramethylammonium hydroxide and 2,5-dinitrophenol in a 1:1 molar ratio were dissolved in water; after several days, pink single crystals formed, which proved to be suitable for single-crystal X-ray diffraction analysis.

Crystal data

$C_4H_{12}N^+\cdot C_6H_3N_2O_5^-\cdot H_2O$
$M_r = 275.27$
Triclinic, $P\bar{1}$
$a = 6.808$ (1) Å
$b = 9.995$ (2) Å
$c = 11.421$ (2) Å
$\alpha = 106.38$ (2)°
$\beta = 104.80$ (2)°
$\gamma = 102.23$ (2)°
$V = 686.3$ (3) Å^3
$Z = 2$
$D_x = 1.332$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1225 reflections
$\theta = 3.2$–28.0°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, pink
0.32 × 0.27 × 0.22 mm

Data collection

Kuma KM-4 diffractometer
ω scans
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min} = 0.963$, $T_{\max} = 0.974$
8043 measured reflections
3291 independent reflections
2196 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 28.0°$
$h = -8 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.064$
$S = 1.00$
3291 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0192P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.037 (2)

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.2677 (13)	N1—O2	1.2109 (13)
C1—C6	1.4235 (16)	N1—O3	1.2176 (13)
C1—C2	1.4264 (16)	N2—O4	1.2078 (13)
C2—C3	1.3816 (15)	N2—O5	1.2091 (13)
C2—N1	1.4397 (16)	N3—C8	1.4711 (16)
C3—C4	1.3616 (16)	N3—C10	1.4732 (17)
C4—C5	1.3857 (15)	N3—C9	1.4764 (16)
C5—C6	1.3534 (15)	N3—C7	1.4776 (15)
C5—N2	1.4785 (16)		
O2—N1—O3	120.15 (13)	C10—N3—C9	110.53 (12)
O4—N2—O5	122.24 (13)	C8—N3—C7	109.32 (11)
C8—N3—C10	109.42 (12)	C10—N3—C7	110.67 (11)
C8—N3—C9	106.68 (12)	C9—N3—C7	110.13 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H61···O1$^{\rm i}$	0.936 (17)	1.868 (17)	2.8021 (15)	174.9 (17)
O6—H62···O1$^{\rm ii}$	0.861 (17)	2.001 (18)	2.8119 (17)	156.5 (17)

Symmetry codes: (i) x, y, z; (ii) $-x + 1, -y + 1, -z + 1$.

Data collection: *KM-4 CCD Software* (Kuma, 2001); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

GJP thanks the CAPES and CNPq foundations (Brazil) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1165). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. & Orpen, A. G. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Andersen, E. K., Andersen, I. G. K. & Plong-Sorensen, G. (1989). *Acta Chem. Scand.* **43**, 624–635.

Desiraju, G. R. (1990). In *Crystal Engineering: The Design of Organic Solids*. Amsterdam: Elsevier.

Frisch, J. M., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A. Jr, Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C. *et al.* (1998). *GAUSSIAN98*. Revision A3. Gaussian Inc., Pittsburgh, PA, USA.

Gillespie, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.

Gillespie, R. J. (1992). *Chem. Soc. Rev.* **21**, 59–69.

Iwasaki, F., Sato, M. & Aihara, A. (1976). *Acta Cryst.* B**32**, 102–106.

Janczak, J. & Perpétuo, G. J. (2004). *Acta Cryst.* C**60**, o211–o214.

Kagawa, T., Kawai, R., Kashino, S. & Haisa, M. (1976). *Acta Cryst.* B**32**, 3171–3175.

Krische, M. J. & Lehn, J. M. (2000). *Struct. Bonding*, **96**, 3–29.

Kuma (2001). *KM-4 CCD Software*. Version 163. Kuma Diffraction, Wrocław, Poland.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 262. Ithaca: Cornell University Press.

Perpétuo, G. J. & Janczak, J. (2003). *Pol. J. Chem.* **77**, 1323–1337.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sherington, D. C. & Taskinen, K. A. (2001). *Chem. Soc. Rev.* **30**, 83–91.