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Benzyltrimethylammonium *p*-Nitrophenolate Trihydrate

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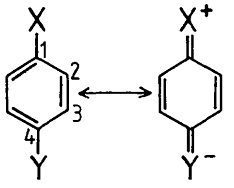
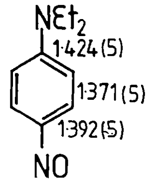
Abstract. $C_{10}H_{16}N^+.C_6H_4NO_3^-.3H_2O$, $M_r = 342{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}160\,(1)$, $b = 10{\cdot}818\,(1)$, $c = 27{\cdot}297\,(3)$ Å, $V = 1819{\cdot}04\,(3)$ Å^3, $Z = 4$, D_m(by flotation) = 1·25 (1), $D_x = 1{\cdot}250$ Mg m^{-3}, $F(000) = 736$, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 0{\cdot}71$ mm^{-1}, $T = 288\,(1)$ K, $R = 0{\cdot}063$ for 1135 observed reflections. Overall, the bond lengths in the *p*-nitrophenolate anion do not indicate a significant contribution from a quinonoid form. The phenolic oxygen is H-bonded to three water molecules in the crystal, O···O distances 2·714 (7)–2·795 (6) Å, and each water molecule is H-bonded to two waters, O···O distances 2·771 (7)–2·834 (7) Å.

Introduction. The possibility of systematic changes with substituent in the aromatic C—C bond lengths in variously substituted benzenes has attracted much attention. A recent analysis of both gas- and solid-phase evidence shows no such systematic change in monosubstituted benzenes (Topsom, 1987). In *p*-disubstituted benzenes (I), where one substituent is π-electron donating and the other π-electron accepting, contributions from the canonical structure (II) should then lead to an increase in the C1—C2 and C3—C4 bond lengths and a decrease in the C2—C3 length. Clear changes are only seen apparently in a few examples where the substituents are very strongly donating and accepting, as shown, for example, in the dimensions for (III) (Talberg, 1977*a*); the mean bond lengths are given in Å.

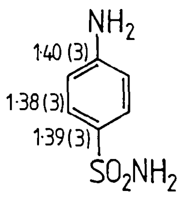


(I) (II)

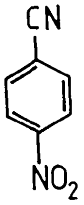


(III)

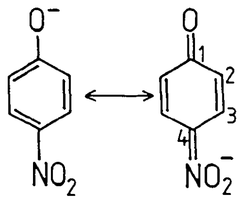
The bond lengths found in compounds such as (IV) (O'Connell & Maslen, 1967) cannot be convincingly used to demonstrate contributions from such quinonoid forms since similar values are found in compounds such as (V) (Higashi & Osaki, 1977), where clearly no such contributions occur. Theoretical calculations (Von Nagy Felsobuki, Topsom, Pollack & Taft, 1982) have also suggested only very limited changes, for example a decrease of only 0·003 Å in C2—C3 in *p*-nitroaniline compared with the expected value based on the corresponding monosubstituted benzenes. Such calculations do, however, suggest larger changes for the *p*-nitrophenoxide ion (VI), where charge is spread in the quinonoid form (VII). The only experimental results available for such phenoxides are for hydrates of *p*-nitrosophenolates containing alkali metal cations (Talberg, 1974, 1975, 1977*b*). We thus wished to look at the *p*-nitrophenolate ion together with a cation that should avoid any counter-ion effect. We report here the results for benzyltrimethylammonium *p*-nitrophenolate which crystallizes as a trihydrate.



(IV)



(V)



(VI) (VII)

Experimental. Colourless prismatic crystals from benzene; crystal *ca* 0·15 × 0·25 × 0·15 mm aligned on a Rigaku-AFC diffractometer; cell parameters determined by least squares from 2θ values for 25 strong reflections; three standard reflections, no significant intensity variation; Cu $K\alpha$ radiation (graphite crystal monochromator); ω–2θ scan, 2θ scan rate 2° min^{-1}, scan range ($\Delta\omega$) 1·2° + 0·5° tanθ, $2\theta_{\max} = 130°$; 1135 of 1780 non-equivalent terms (h 0–7, k 0–12, l 0–32) with $I \geq 1{\cdot}5\sigma(I)$ used; intensities corrected for absorption (transmission factors ranged from 0·908 to 0·877); four large terms apparently seriously affected by extinction omitted from final refinement. Structure solved by direct methods with *SHELX*76 (Sheldrick, 1976). Apart from the H atoms of the methyl substituents, which were included at idealized positions, and those of the water molecules, which were omitted from the analysis, the H-atom sites were located on difference maps. Refinement, with anisotropic temperature factors for C, N and O atoms, and isotropic for H atoms, converged at $R = 0{\cdot}063$ and $wR = 0{\cdot}058$; max. Δ/σ 0·04 for non-H atoms and 0·13 for H atoms;

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largest peaks on final difference map +0·22 and −0·22 e Å^{-3}; the function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma^2|F_o| + 0{\cdot}0004|F_o|^2)^{-1}$. Scattering factors for O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections with values of Cromer & Liberman (1970).

Discussion. Final atomic coordinates of the non-hydrogen atoms are given in Table 1;* Fig. 1, which contains the atom numbering, and Fig. 2 have been drawn with *ORTEP* (Johnson, 1976). Perspective drawings of the cation and anion are illustrated in Fig. 1 and bond lengths are given in Table 2.

Table 1. *Final atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2 U_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}(Å^2)
C1	4564 (12)	4517 (7)	8622 (3)	2·4 (3)
C2	2446 (14)	4931 (7)	8745 (3)	3·8 (3)
C3	1636 (12)	4826 (8)	9211 (3)	3·8 (3)
C4	2878 (12)	4273 (6)	9572 (3)	3·3 (3)
C5	4948 (13)	3869 (8)	9471 (3)	4·0 (3)
C6	5828 (13)	4009 (7)	9003 (3)	3·4 (3)
O7	5338 (8)	4644 (4)	8181 (1)	4·0 (2)
N8	1965 (14)	4106 (7)	10058 (2)	4·7 (3)
O9	134 (11)	4495 (6)	10132 (2)	6·6 (3)
O10	3069 (10)	3599 (5)	10370 (2)	6·2 (3)
C11	1156 (12)	−1403 (7)	8941 (2)	3·4 (3)
C12	−26 (14)	−2145 (7)	8625 (3)	3·5 (3)
C13	−1880 (15)	−2756 (8)	8779 (3)	4·9 (3)
C14	−2551 (14)	−2631 (7)	9268 (3)	4·5 (3)
C15	−1311 (16)	−1939 (8)	9591 (3)	4·8 (3)
C16	502 (14)	−1323 (7)	9429 (3)	3·9 (3)
C17	3262 (12)	−803 (7)	8779 (3)	3·4 (3)
N18	2982 (9)	459 (5)	8536 (2)	3·1 (2)
C19	5254 (12)	967 (7)	8450 (3)	4·7 (3)
C20	1823 (13)	337 (7)	8050 (2)	4·6 (3)
C21	1780 (13)	1323 (7)	8862 (3)	4·5 (3)
O*W*1	1577 (8)	7981 (4)	7136 (2)	4·7 (2)
O*W*2	4555 (9)	7021 (4)	7821 (2)	5·3 (2)
O*W*3	7499 (8)	8778 (5)	7498 (2)	5·2 (2)

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

C1–C2	1·420 (11)	C11–C12	1·385 (11)
C1–C6	1·411 (11)	C11–C16	1·394 (10)
C1–O7	1·302 (9)	C11–C17	1·517 (10)
C2–C3	1·371 (12)	C12–C13	1·385 (12)
C3–C4	1·384 (11)	C13–C14	1·404 (12)
C4–C5	1·376 (11)	C14–C15	1·386 (12)
C4–N8	1·452 (10)	C15–C16	1·374 (13)
C5–C6	1·396 (12)	C17–N18	1·528 (9)
N8–O9	1·221 (11)	N18–C19	1·522 (9)
N8–O10	1·220 (9)	N18–C20	1·512 (8)
		N18–C21	1·489 (10)

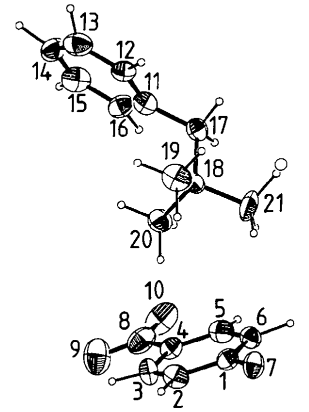

Fig. 1. Perspective views of the molecular ions with thermal ellipsoids at the 40% probability level.

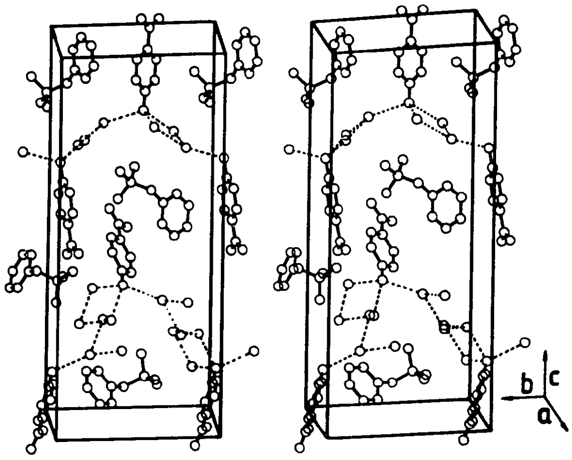

Fig. 2. Stereoview of the crystal packing.

Table 3. *Mean bond lengths* (Å) *for p-nitrophenols and related structures* [*numbering as in* (VII)]

Compound	C1–C2	C2–C3	C3–C4	C1–O	C4–N	N–O	Mean e.s.d.	Reference
p-Nitrophenol α-modification	1·386	1·379	1·390	1·351	1·442	1·234	0·006	Coppens & Schmidt (1965*a*)
p-Nitrophenol β-modification	1·390	1·375	1·386	1·352	1·446	1·225	0·002	Coppens & Schmidt (1965*b*)
p-Nitroso-phenolate K salt, H_2O	1·47	1·36	1·43	1·24	1·27		0·03	Talberg (1974)
p-Nitroso-phenolate Na salt, $3H_2O$	1·448	1·356	1·429	1·259	1·340		0·014	Talberg (1975)
p-Nitroso-phenolate Mg salt, $6H_2O$	1·438	1·363	1·423	1·281	1·359		0·002	Talberg (1977*b*)
p-Nitroanisole	1·401	1·361	1·387	1·351	1·450	1·232	0·005	Talberg (1978)
p-Nitrophenolate–Benzyltrimethylammonium salt, $3H_2O$	1·416	1·383	1·380	1·302	1·452	1·221	0·011	Present study

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* Lists of structure amplitudes, anisotropic temperature factors, H-atom parameters, bond angles, hydrogen-bond distances and short intermolecular contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43689 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure obtained shows that the benzyltrimethylammonium cation does not lie close to the phenolic oxygen atom (see Fig. 2) and is thus an appropriate cation for the study. The phenolic oxygen is, however, hydrogen-bonded to three water molecules [O···O distances 2·756 (7), 2·795 (6), 2·714 (7) Å] and, in turn, each water molecule is further hydrogen-bonded to two waters at distances of 2·818 (7), 2·834 (7) and 2·771 (7) Å.*

Although the C1—O bond length of 1·302 (9) Å indicates a significant double-bond character, the C4—N bond length of 1·452 (10) Å and the mean lengths C1—C2 1·416 (11), C2—C3 1·383 (12) and C3—C4 1·380 (11) Å which lie within 2σ of the values reported for these lengths in the *p*-nitrophenols and *p*-nitroanisole (see Table 3), do not indicate a significant contribution of the quinonoid form (VII).

It would thus appear that the three water molecules that are hydrogen-bonded to the nitrophenolate anion significantly reduce the negative charge on the oxygen atom and so lead to a decreased need to spread the charge into the ring. Work is proceeding in an attempt to produce the anhydrous salt of benzyltrimethylammonium *p*-nitrophenolate for further study.

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* See deposition footnote.

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Structure of 1,2,3,3a-Tetrahydro-3a,7-diphenyl-5-(*p*-tolyl)pyrazolo[1,5-*a*]pyridine-3-carbonitrile

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Abstract. $C_{27}H_{23}N_3$, $M_r = 389{\cdot}5$, monoclinic, $P2_1$, $a = 8{\cdot}783$ (1), $b = 11{\cdot}988$ (2), $c = 10{\cdot}961$ (1) Å, $\beta = 111{\cdot}26$ (1)°, $V = 1075{\cdot}5$ (3) Å^3, $Z = 2$, D_m(flotation) = 1·19 (2), $D_x = 1{\cdot}202$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}2$ cm^{-1}, $F(000) = 412$, $T = 292$ K. Final $R = 0{\cdot}033$ for 1498 observed reflections. The compound has two non-planar *cis*-fused heterocycles. The six-membered heterocycle adopts a sofa conformation due to the participation of the nitrogen atom's lone pair in the diene conjugated system. The five-membered ring shows an envelope conformation and a torsionally strained C—C bond [central C—C = 1·582 (4) Å in anticlinal φ—C—C—CN].

Introduction. From the reaction of the 1-amino-2,4,6-triphenylpyridinium ion (1) with a variety of reactives, Katritzky, Grzeskowiack. Alajarin-Ceron, bin Bahari, Beltrami & Keay (1982) reported the synthesis of some 60 novel derivatives (2,3,4). Unique among the products obtained was (5), which resulted from cycloaddition of acrylonitrile to (1), in spite of the steric impediment imposed by the flanking Ph groups.

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