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Nitrate salt of protonated 2-(diethylaminomethyl)phenol

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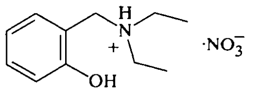
Abstract

In the title compound, diethyl(2-hydroxybenzyl)ammonium nitrate, $C_{11}H_{18}NO^+\cdot NO_3^-$, the mean value of the C—N—C angles in the protonated amino side chain (112.1°) is *ca* 3° greater than that observed for nonprotonated units. The C—O distance [1.356(2) Å] is typical of an aromatic C—OH bond.

Comment

Phenol derivatives containing one or two $-CH_2NR_2$ side chains are versatile multidentate ligands, stabilizing a variety of mono- and polynuclear complexes. We recently prepared complexes with first-row transition M^{2+} ions and found that the ligand coordinated as a phenolate donor, the proton being shifted onto the amino group (Connac *et al.*, 1997; Habbadi *et al.*, 1999; Habbadi *et al.*, 1998). Since examples of these ligands coordinating as a non-deprotonated phenol have also been reported (Hogerheide *et al.*, 1996), we felt that reliable diagnostic features were needed to ascertain the protonation state of the potential donors. This would be especially useful in the case of heavy-metal complexes, where H atoms are often difficult to locate unambiguously from X-ray data. To this end, the structure of the title compound, (I), was studied using X-ray crystallography.



(I)

The asymmetric unit of (I) includes the nitrate anion and the ammonium cation, as shown in Fig. 1. Bond lengths and angles are listed in Table 1. Compound (I), considering its stoichiometry, must contain a C—OH group and a protonated $-CH_2NHR_2^+$ side chain. This is confirmed by the presence of well defined electron-density peaks for these H atoms in the difference Fourier

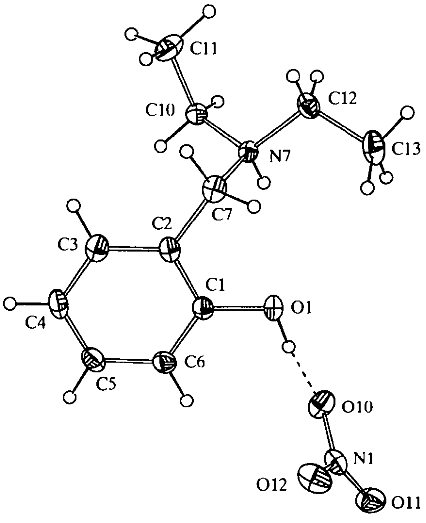


Fig. 1. *ORTEPII* (Johnson, 1976) drawing of the title compound, showing the atom-numbering scheme. Displacement ellipsoids correspond to 50% probability, and H atoms are represented by spheres of arbitrary radii. The dashed line corresponds to a hydrogen bond.

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map, and by the reasonable positional and displacement parameters obtained by refinement.

Two structural features are worthy of discussion. For an Na^+ complex with 2,6-bis(dimethylaminomethyl)-4-methylphenol, in which both neutral and deprotonated phenol groups are coordinated, Hogerheide *et al.* (1996) pointed out that the C—OH bond (1.372 Å) is appreciably longer than C—O^- (1.301 Å). The distance of 1.356 (2) Å observed in (I) is in good agreement with this C—OH bond length. On the other hand, the protonation state of the side chain can be deduced from the C—N—C angles. Inspection of samples, including 23 free and 61 coordinated –CH_2NR_2 groups found in the Cambridge Structural Database (1998), reveals that the mean of the three C—N—C angles does not differ significantly between these two types of groups, the average value being 108.9° for both samples (Habbadi *et al.*, 1999). The mean value observed here for the C—N—C angles (112.1°) is definitely higher, and comparable with those found in related complexes containing protonated side chains (111.7–113.0°; Connac *et al.*, 1998; Habbadi *et al.*, 1998, 1999). Therefore, although the C—N—C angles may be individually affected by local strain, their mean value provides a reliable diagnostic to distinguish protonated from non-protonated amino groups. The rest of the molecule shows no unusual features.

The two types of ions are connected by hydrogen bonds, generating an infinite chain along the *a* axis. The hydroxyl group forms a strong hydrogen bond with O10 [O1···O10 = 2.663 (2) Å and O1—H1···O10 = 173 (2)°]. The NH protons interact more weakly, forming a bifurcated hydrogen bond with O10 [N7···O10 = 3.025 (2) Å] and O11 [N7···O11 = 3.054 (2) Å].

Experimental

The compound was isolated while attempting to prepare a Gd^{III} complex by adding the neutral organic ligand and NEt_3 to a solution of anhydrous $Gd(NO_3)_3$ in 1:1 tetrahydrofuran/ethanol. Solvent evaporation and workup with hexane–ether yielded a white powder. Colourless crystals of (I) were obtained by recrystallization in dichloromethane. The compound can also be prepared by evaporation of a dilute 1:1 ligand/HNO_3 solution in tetrahydrofuran.

Crystal data

$C_{11}H_{18}NO^+\cdot NO_3^-$
$M_r = 242.274$
Orthorhombic
Pbca
$a = 10.0090 (13)$ Å
$b = 15.472 (2)$ Å
$c = 16.216 (2)$ Å
$V = 2511.3 (5)$ Å^3
$Z = 8$
$D_x = 1.282$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.0–13.6°$
$\mu = 0.098$ mm^{-1}
$T = 160 (3)$ K
Prism
0.24 × 0.22 × 0.19 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: none
15 341 measured reflections
2004 independent reflections
1384 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 26°$
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -20 \rightarrow 20$
5 standard reflections
frequency: 60 min
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.082$
$S = 1.209$
2004 reflections
226 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.3071P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.009$
$\Delta\rho_{\rm max} = 0.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.356 (2)	C1—C2	1.405 (3)
O10—N1	1.268 (2)	C2—C3	1.382 (3)
O11—N1	1.242 (2)	C2—C7	1.495 (3)
O12—N1	1.239 (2)	C3—C4	1.389 (3)
N7—C12	1.505 (3)	C4—C5	1.381 (3)
N7—C10	1.510 (2)	C5—C6	1.385 (3)
N7—C7	1.518 (3)	C10—C11	1.501 (3)
C1—C6	1.391 (3)	C12—C13	1.511 (3)
O12—N1—O11	122.2 (2)	C3—C2—C7	122.4 (2)
O12—N1—O10	119.9 (2)	C1—C2—C7	118.7 (2)
O11—N1—O10	117.9 (2)	C2—C3—C4	121.2 (2)
C12—N7—C10	112.3 (2)	C5—C4—C3	119.1 (2)
C12—N7—C7	111.6 (2)	C4—C5—C6	121.2 (2)
C10—N7—C7	112.3 (2)	C5—C6—C1	119.3 (2)
O1—C1—C6	123.2 (2)	C2—C7—N7	111.9 (2)
O1—C1—C2	116.5 (2)	C11—C10—N7	114.0 (2)
C6—C1—C2	120.2 (2)	N7—C12—C13	112.1 (2)
C3—C2—C1	118.9 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O10	0.93 (3)	1.74 (3)	2.663 (2)	173 (2)
N7—H7···O10$^{\rm i}$	0.89 (2)	2.45 (2)	3.025 (2)	123.0 (15)
N7—H7···O11$^{\rm i}$	0.89 (2)	2.24 (2)	3.054 (2)	151.4 (16)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

The orthorhombic Laue symmetry and systematic absences identified the space group unambiguously. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985), and difference map syntheses using *NRCVAX* (Gabe *et al.*, 1989) and *SHELXL*96 (Sheldrick, 1996). All non-H atoms were refined anisotropically, while H atoms were refined isotropically. The following means, ranges and s.u.'s (on individual parameters) were obtained for the H atoms: $U_{\rm iso}$(methyl) (Å^2): 0.068, 0.051–0.076 ($\sigma = 0.008$); $U_{\rm iso}$(other C—H) (Å^2): 0.042, 0.034–0.051 ($\sigma = 0.007$); C—H distances (Å): 0.098, 0.092–1.05 ($\sigma = 0.003$).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC Crystallographic Computer Programs* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *SHELXL*96. Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1426). Services for accessing these data are described at the back of the journal.

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tert-Butylammonium hydrogen phenyl phosphate

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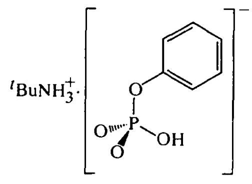
Abstract

The title compound, (Me$_3$C)NH$_3^+$·PhOPO$_3$H$^-$, contains hydrogen phenyl phosphate anions connected by electrostatic interactions and hydrogen bonds to *tert*-butylammonium cations, forming a two-dimensional network.

Comment

There are three structurally characterized phenyl phosphate salts with inorganic cations (Svetich & Caughlan, 1963; Caughlan & ul Haque, 1967; Glowiak & Wnek, 1985) and only one with an organic cation (Kneeland *et al.*, 1993). Three examples of hydrogen phenyl phosphate salts have been structurally characterized (Kennard *et al.*, 1967; Glowiak & Szemik, 1986; Kral *et al.*, 1996). The present study of the title compound, (I), was undertaken in order to obtain a deeper insight into the effect of the cation on the crystal packing, the strength of the intermolecular contacts and the chemical properties of organoammonium phenyl phosphates.



(I)

The asymmetric unit of the title compound (Fig. 1) contains one C$_6$H$_6$PO$_4^-$ anion and one C$_4$H$_{12}$N$^+$ cation. The hydrogen phenyl phosphate anions form dimeric units through the strong O1—H1···O3 hydrogen bond [2.5912 (16) Å]. The interaction between these dimers takes place through three hydrogen bonds involving the NH$_3^+$ group of the *tert*-butylammonium cations. This hydrogen-bond network generates a two-dimensional structure (Fig. 2), with the layers parallel to the (10$\bar{1}$) plane and each layer containing a hydrophilic central zone formed by the terminal O atoms and the NH$_3^+$ group. The aromatic rings and methyl groups emerge above and below this central zone to form the corresponding hydrophobic zone with the adjacent layers (Fig. 3).

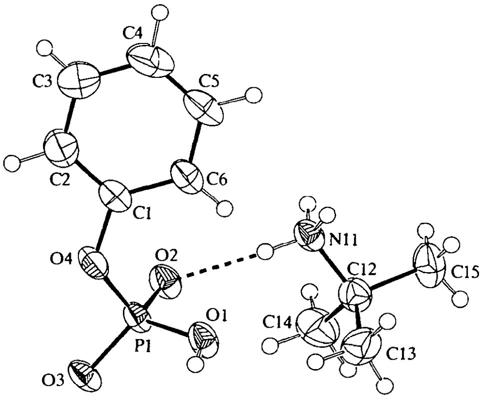


Fig. 1. View of *tert*-butylammonium hydrogen phenyl phosphate, showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as spheres of an arbitrary radius. The dashed line indicates a hydrogen bond.

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