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Inclusion of $HNEt_3^+$ in an acyclic tetraphenolate

Pascal C. Leverd,[a]* Dirk Weber,[b] Wolf D. Habicher[b] and Martine Nierlich[a]

[a]CEA/Saclay, Service de Chimie Moléculaire, Bâtiment 125, 91191 Gif-sur-Yvette CEDEX, France, and [b]Institut für Organische Chemie, Technische Universität Dresden, Mommsenstrasse 13, D-01062, Dresden, Germany
Correspondence e-mail: leverd@drecam.cea.fr

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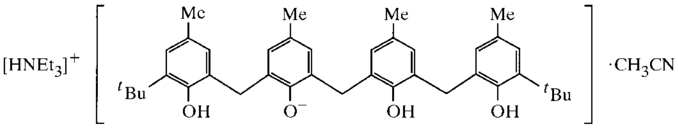
The acyclic tetraphenolic derivative 2,2′-methylenebis[6-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenol] reacts with excess triethylamine in acetonitrile to form a molecular complex, *i.e.* triethylammonium 2-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-6-[3-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-2-hydroxy-5-methylbenzyl]-4-methylphenolate acetonitrile solvate, $C_6H_{16}N^+\cdot C_{39}H_{47}O_4^-\cdot C_2H_3N$, where the organic $HNEt_3^+$ cation is included in the partial cone defined by the aromatic faces of the acyclic polyphenolate.

Comment

The separation of radioactive metal cations from waste solutions produced by the nuclear industry is an important goal for the environmental management and recycling of nuclear fuels. In this respect, the comparative study of various classes of complexing agents has been undertaken, in particular, the calixarenes and their acyclic counterparts. The latter are very flexible ligands which have the potential to fit the coordination requirements of actinide cations (Thuéry & Nierlich, 1997). Full characterization of the organic extractants, including determination of their conformation in the solid state, is important for the understanding of extraction processes. If there are now numerous examples of crystal structures of calix[4]arenes reported in the literature, those of their acyclic homologues are less common (Casiraghi *et al.*, 1982; Paulus & Böhmer, 1984; Usui *et al.*, 1991). All these reports concern the fully protonated ligands. We present herein the crystal structure of the acetonitrile solvate of the triethylammonium salt of 2,2′-methylenebis[6-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenol], (I), the first crystal structure report of an anionic derivative of an acyclic tetraphenol.



(I)

The crystal structure of (I) (Fig. 1) reveals that the tetraphenolic derivative has been deprotonated once by reaction with excess triethylamine and that the anion formed is stabilized by strong intramolecular hydrogen bonds. The triethylammonium cation donates a hydrogen bond to the deprotonated O3 phenolate group. Two other hydrogen bonds are donated to O3 by O2 and O4, while O2 receives one from O1. This arrangement is reminiscent of the hydrogen-bond pattern classically stabilizing the deprotonated calix[4]arene (Gutsche, 1998).

The conformation of (I) in the solid state can be described as *syn–anti* (Casiraghi *et al.*, 1982; Perrin & Oehler, 1990). Consequently, three of its aromatic faces are organized into a partial cone. This cavity is occupied by one of the terminal methyl groups of a triethylammonium cation hydrogen bonded to an adjacent phenolate (Fig. 2). This methyl group is positioned 1.17 (2) Å below the plane defined by the lips of the partial cone (C28, C38 and C48) that can be considered as the limit of the cavity. Interestingly, the inclusion of cations in the aromatic cavity of calix[4]arenes is a well known feature of this class of macrocycles (Leverd *et al.*, 2000). Conversely, the formation of host–guest complexes of acyclic oligomers (induced-fit inclusion) has only been evidenced for neutral organic molecules (Sone *et al.*, 1989; Usui *et al.*, 1991) and not for charged species. Compound (I) is, to the best of our knowledge, the first example of such an inclusion occurring with a cation.

The extended structure (Fig. 2) consists of residues organizing the solid into rods parallel to the [010] direction. In contrast to previously reported structures of polyphenolic oligomers which pack into hydrogen-bonded dimers or infinite

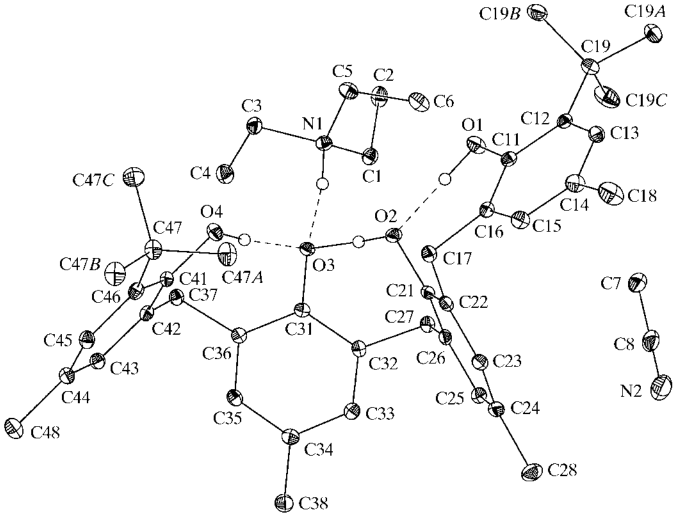


Figure 1
Drawing of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 20% probability level except for the H atoms which are represented as spheres of arbitrary radii. H atoms which do not participate in hydrogen bonding have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

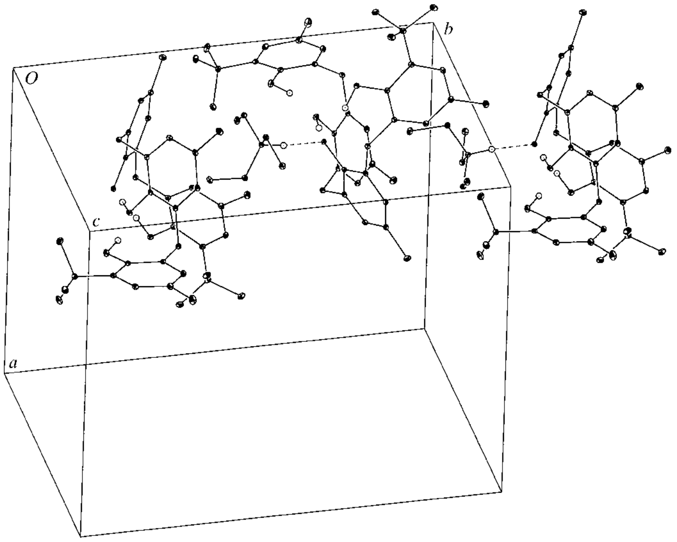


Figure 2
View of the extended structure of (I).

chains, the arrangement of the solid in (I) results from interactions due to both hydrogen bonds and inclusion phenomena.

Experimental

The tetraphenol was synthesized according to a published method (Weber *et al.*, 1999). Single crystals of the title compound suitable for structure determination were obtained by slow evaporation (298 K) of an acetonitrile solution containing a mixture of the tetraphenol and a twofold excess of triethylamine.

Crystal data

$C_6H_{16}N^+ \cdot C_{39}H_{47}O_4^- \cdot C_2H_3N$
$M_r = 723.02$
Monoclinic, $P2_1/n$
$a = 16.024\ (3)$ Å
$b = 17.073\ (3)$ Å
$c = 16.067\ (3)$ Å
$\beta = 106.75\ (3)°$
$V = 4209.1\ (15)$ Å^3
$Z = 4$
$D_x = 1.141$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from all reflections
$\theta = 2.73–26.37°$
$\mu = 0.071$ mm^{-1}
$T = 100\ (2)$ K
Block, colourless
0.20 × 0.20 × 0.15 mm

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.96 (3)	1.74 (3)	2.684 (2)	166 (2)
O2—H2···O3	1.04 (3)	1.46 (3)	2.499 (2)	177 (2)
O4—H4···O3	1.00 (3)	1.68 (3)	2.666 (2)	167 (2)
N1—H3···O3$^{\rm i}$	0.98 (3)	1.70 (3)	2.671 (3)	170 (2)

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

Data collection

Nonius CCD diffractometer
ω scans
15352 measured reflections
8472 independent reflections
5631 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\rm max} = 26.37°$
$h = 0 \rightarrow 19$
$k = -21 \rightarrow 21$
$l = -20 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.123$
$S = 0.997$
8472 reflections
508 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.8636P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

H atoms of the ligand were included as riding atoms at calculated positions (U = 1.2 times that of the corresponding carbon) with the exception of those involved in hydrogen bonding which were positioned from the Fourier difference map and refined.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1087). Services for accessing these data are described at the back of the journal.

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