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Cation–anion CH···O⁻ interactions in the metal-free phenolate, tetra-*n*-butylammonium phenol-phenolate

Richard Goddard, H. Martin Herzog and Manfred T. Reetz*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

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Abstract—Deprotonation of phenol by tetra-*n*-butylammonium hydroxide and subsequent removal of water by P_2O_5 results in quantitative formation of tetra-*n*-butylammonium phenol-phenolate. The compound crystallizes as an ion pair, with the solute phenol molecule intimately attached to the phenolate anion by an $O-H\cdots O^-$ hydrogen bond ($O\cdots O$ 2.471(5) Å). A short contact between one α-C atom of the tetra-*n*-butylammonium cation and the phenolate O atom indicates that the ion pair interaction is strengthened by an additional $C-H\cdots O^-$ hydrogen-bond, despite the attached phenol. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The vast majority of structures of alkali metal and alkaline earth phenoxides are characterized by extended aggregates in which the phenolate anion is intimately bound up with the metal. Often the presence of sterically bulky ligands is necessary for the preparation of distinct molecular species, and in many cases the strong ionic interactions between the negatively charged O atom of the phenoxide and the positively charged metal ions force the phenolate anions to adopt μ_2-bridging,[1] μ_3-face-bridging,[2] and in the case of NaOPh·THF, μ_4-sites.[3] So strong is the attraction between the phenolate anion and the alkali metals that a terminally bonded phenolate has only been observed in a complex containing a sodium cation otherwise bonded to an 18-crown-6-ether ligand.[4]

Unless mediated by solvents or ligands the formation of the aggregates is so uncontrolled that crystals with a definite stoichiometry suitable for X-ray analysis are often difficult to prepare and in some cases the structures of the compounds have only been determined from powder diffraction data.[5,6] In C_6H_5OM (M=Li, Na, K, Rb, Cs), for example, the electropositive metals have such an affinity for the phenolate anion that there are indications of additional bonding interaction between the metal cation and the C atoms of the phenyl ring.[5] Such interactions have been suggested as the cause of the activation of the phenyl ring in the Kolbe–Schmitt solid–gas direct carboxylation of alkalimetal phenolates by CO_2 to give salicylic acid.[3,6]

In contrast, the interaction between the phenolate anion and the tetra-*n*-butylammonium cation appears to be completely different. Calculations show that in the same solvent the cation–anion interaction energy is much weaker with the tetra-*n*-butylammonium cation (2.4 kcal mol^{-1}) than with Na^+ (4.5 kcal mol^{-1}).[7] Kinetic investigations on the nucleophilic attack of the phenolate anion on butyl halides in aprotic solvents have shown that the rate of the reaction depends strongly on the counterion, with the reactions involving the tetra-*n*-butylammonium cation proceeding much faster than those with K^+. Moreover, whereas the rate constants with K^+ depend greatly on the dielectric constant of the solvent, with the tetra-butylammonium cation they do not.[8] Indeed, tetra-*n*-butylammonium bromide has been shown to have catalytic effect on the O-alkylation of phenol by benzyl halides by KF in DMF under solid–liquid phase transfer conditions.[9]

Here we describe the preparation of the metal-free phenolate, tetra-*n*-butyl-ammonium phenol-phenolate, and the determination of its crystal structure. We undertook the work in order to establish whether the salt would contain the free phenolate anion, or whether it would in fact undergo self-association, similar to that observed for tetra-*n*-butylammonium-1-cyano-1-phenylethanide, in which the N atoms of two cyanophenylethanide ions take up bridging positions between two tetra-*n*-butylammonium cations to form a supramolecular ion pair.[10]

2. Results and discussion

Our interest in the structure of the metal-free phenolate, tetra-*n*-butylammonium phenol-phenolate, stemmed from the observation that the carbanions formed by the deprotonation by tetra-*n*-butylammonium hydroxide of

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Keywords: tetra-*n*-butylammonium phenol-phenolate; ion pair interaction; metal-free phenolate.

* Corresponding author. Tel.: +49-208-306-2000; fax: +49-208-306-2985; e-mail: reetz@mpi-muelheim.mpg.de

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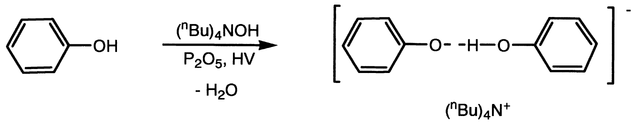
C–H and N–H acid compounds, such as malonates or nitriles,[11] are not free carbanions, as first thought,[12] but rather supramolecular ion pairs involving O···H–C or N···H–C hydrogen bonds between the electronegative atoms in the anions and the acidic C–H bonds of the α-C-atoms of the tetra-butylammonium cations.[13–15] Since phenol is more acidic than these compounds, we expected the anion–cation interaction to be weaker and possibly completely absent.

Tetra-*n*-butylammonium phenol-phenolate was prepared by reaction of two equivalents of phenol with one of tetra-*n*-butylammonium hydroxide in a method similar to that originally described by Nielsen and Hammerich, except that the water was removed by phosphorus pentoxide, instead of azeotropic distillation with cyclohexane under reduced pressure[16] (Scheme 1).



Scheme 1.

Care was taken to ensure that the compound was kept free from protic solvents, and crystals were grown from dimethylformamide.

The results of the X-ray analysis are summarized in Fig. 1, which shows that the salt contains the phenol-phenolate anion. Attempts to prepare the phenol-free salt were unsuccessful, and in all cases the phenol-phenolate anion was obtained. Although the anion initially appears symmetrical, with PhO groups at both ends of the fragment, the bridging H atom, H, is clearly attached to O2, and thus there is no ambiguity about the location of the negative charge. H was located in a difference Fourier synthesis that was calculated with all other atoms, including H atoms, present in the structure, and it refined well with a final displacement parameter of $U_H=0.07(2)$ Å^2. This is somewhat larger than that of the atom to which is attached ($U_{O2}(iso)=0.0479(8)$ Å^2), but that is to be expected for a terminal atom. The O2–H distance of 0.90(7) Å is nevertheless normal, and the O1···H–O2 hydrogen bond is almost linear (175(2)°). The C–O distances from the phenyl ring to the O atom in the two PhO moieties are also in accord with the assignment, since the C–O distance in the phenolate anion O1–C17 at 1.316(5) Å is significantly shorter than that in the phenol molecule (O2–C23 1.342(6) Å). This latter bond is shorter than that oberved in pure phenol at 123 K (C–O$_{average}$=1.372(6) Å),[17] presumably as a consequence of the weaker O–H bond due to the stronger O–H···O^- bond to the phenolate anion.

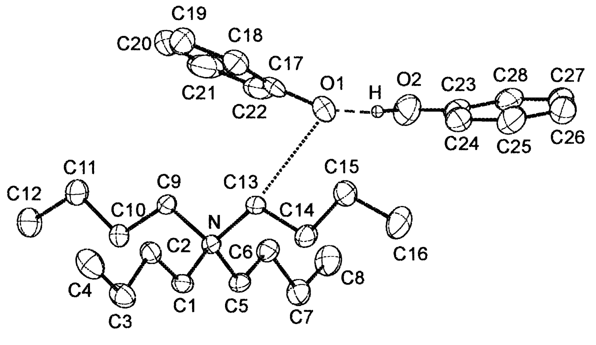


Figure 1. Molecular structure of tetra-*n*-butylammonium phenol-phenolate, showing C–H···O^- (dotted) and O–H···O^- (dashed) H-bonding interactions.

The O···O distance in the phenol-phenolate moiety at 2.471(5) Å is also significantly shorter than the average O···O distance in phenol, which is 2.68(2) Å.[17] The torsion angle C17–O1···O2–C23 is not 180° as one might expect for an isolated system but 154.6°. This is likely to be the result of an additional C–H···O^- hydrogen bonding interaction between the the phenolate O atom and one α-C atom of the tetra-butylammonium cation. The corresponding O···C distance of 3.340(5) Å (O1···C13) is significantly longer than that in 1,3-dimesitylimidazolium 2,6-di-*tert*-butyl-4-methylphenolate, which at 2.801(4) Å is thought to be the shortest observed to date,[18] but it lies in the middle of the range for similar X···H–C interactions found in the structures of various supramolecular ion pairs (3.26–3.44 Å).[13,14] The angles around C13 also support the formulation of a C–H···O interaction, since the N–C13···O1 and C14–C13···O1 angles (average 110°) are close to those one would expect for a linear C–H···O^- bond. It appears therefore that the phenol-phenolate anion and the tetra-*n*-butyl-ammonium cation form an intimate ion pair held together by a C–H···O^- hydrogen bond.

At first sight the situation is mirrored in the structure of the Pd phenolate, 1-aqua-1-(hydrogen-tris(pyrazol-1-yl)-borate)-1-pallada(IV)cyclopentane phenol phenolate, which is also a three component system comprising a cation, a phenolate anion and a solvate phenol molecule in close contact with one another.[19] However, in the latter case it is the O^-···H–O hydrogen bond to the water molecule on the cation (2.465 Å) that is significantly shorter than the O^-···H–O hydrogen bond to the solvate phenol molecule (2.645 Å), in accord with the expected affinity of the phenolate anion for the cation.

An analogous arrangement is found in the structure of benzyl dimethyl-(2-hydroxy-3-phenoxypropyl)ammonium phenolate monohydrate solvate, another three component system, in which the O^-···O distance between the phenolate O atom and the β-hydroxy group of the substituted ammonium cation at 2.514 Å is shorter than the O^-···O distance to the solvate molecule (in this case H_2O, 2.698 Å).[20]

In both these cases, hydrogen bonding to the cation appears to take preference over hydrogen bonding to a solvate molecule. In tetra-*n*-butylammonium phenol-phenolate, however, the contrary is true. Clearly, the absence of a suitable hydrogen bond donor on the tetrabutylammonium cation prevents it from functioning as the major hydrogen bond donor.

Despite the interaction between C13 and O1, the alkyl groups of the tetra-*n*-butylammonium cations adopt the all-*trans* conformation, and the C atoms of the trans *n*-butyl groups are essentially coplanar with the N atom (rms deviation: 0.05 Å (N, C1–C8) and 0.03 Å (N, C9–C16)). The *n*-butyl groups pack together in the crystal so that the tetra-butylammonium cations and phenol-phenolate anions occupy alternating aprotic and protic layers. Apart from the interactions between the cation and the anion, and between the anion and the solvate phenol molecule, there appears to be no other significant short contacts in the structure. This is in stark contrast to the structure of sodium phenolate·2(phenol), revealed to be the only compound in the phase diagram of the sodium phenoxide/phenol system, in which the phenolate and two phenol molecules are strongly bound to sodium atoms and one another.[21] Interestingly, among the sodium phenolates it is only in the structure of $C_6H_5ONa{\cdot}3H_2O$ that the O atom of the phenolate ion does not participate in the coordination to the sodium atom, and this has been explained in terms of solvation enthalpies.[22]

3. Conclusions

Deprotonation of phenol with tetra-*n*-butylammonium hydroxide over P_2O_5 results in the formation of crystals of tetra-*n*-butyl ammonium phenol-phenolate, in which a phenol molecule is intimately bound to the phenolate anion. All attempts to prepare the phenol-free salt were unsuccessful. In spite of the presence of the H-bond to a phenol molecule, the phenolate anion is $C{-}H{\cdots}O^-$ hydrogen bonded to one of the α-C atoms of the tetrabutylammonium cation, indicating that the cation–anion $C{-}H{\cdots}O^-$ interaction is also possible in protic solvents. The present structural results and previous crystallographic data concerning tetraalkylammonium salts[10,11,13,14] of enolates and other 'carbanions' may be of help in designing chiral phase transfer catalysts.[23]

4. Experimental

4.1. General

FT-IR spectra were recorded on a Perlin–Elmer 1600 spectrophotometer. ^1H and ^{13}C NMR specta were recorded on a Bruker WH 400 spectrometer at 400 MHz and a Bruker AC 300 spectrometer at 300 MHz.

Chemical shifts are expressed in ppm relative to trimethylsilane as internal standard and *J* values are expressed in Hz. All reactions were undertaken in glass apparatus that had been thrice evacuated by oil pump and flushed with argon. Commercial reagents with a purity of greater than 97% were dried before use, otherwise distilled, recrystallized or sublimed. Tetrahydrofuran (THF) was dried over KOH and CaH_2, then refluxed and distilled over $LiAlH_4$ and triphenylmethane. Dimethylformamide (DMF) was refluxed at 60°C and 25 mbar for 3 days with Desmodur® and dibutyl-tin dilaurate, and subsequently distilled using a 30 cm silvered condenser.

4.1.1. Tetra-*n*-butylammonium phenol-phenolate. To 10 mmol (0.94 g) phenol dissolved in 10 ml THF were added 5 ml of a 1 M tetra-*n*-butylammonium hydroxide solution in methanol and the solvent mixture removed by vacuum. After 60 h at rt under oil-pump vacuum in the presence of phosporus pentoxide, tetra-*n*-butylammonium phenol-phenolate was obtained in quantitative yield. Suitable crystals for an X-ray analysis were obtained by dissolving the residue in dimethyl formamide at 40°C and cooling the saturated solution from 20 to −20°C at a rate of 0.5°C/h. 73% isolated yield; IR (KBr): no N–H absorption, broad H-bond absorption between 2080–2800 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6): δ (ppm) 1.05 (t, CH_3, 12H), 1.48 (tq, CH_2, 8H), 1.76 (m, CH_2, 8H), 3.32 (m, CH_2, 8H), 6.31 (t, 1H), 6.42 (d, 2H), 7.0 (t, 2H); ^{13}C NMR (50 MHz, DMSO-d_6): δ (ppm) 13.3, 19.0, 22.9, 57.3, 117.0, 128.4. Anal. Calcd for $C_{28}H_{47}NO_2$ (429.7): C, 78.27; H, 11.02; N, 3.26. Found: C, 56.7; H, 10.54; N, 4.00.

4.2. X-Ray crystallographic structure determination

The crystal used for the X-ray analysis was mounted on a glass rod and cooled by a cold N_2 gas stream. The structure was solved by Direct Methods,[24,25] and refined by full-matrix least-squares, where the quantity minimized was $[\sum w(F_o^2-F_c^2)^2]$.[25] Non-H atoms were refined anisotropically, and apart from H attached to O2 of the solvate phenol molecule, which was refined with an isotropic atomic displacement parameter (U_H=0.07(2) Å^2), H atoms were included in the refinement using a riding model. Refinement of all the H atoms converged at C13–H13b···O1 167(2)° (C13–H13b 0.91(4) Å; H13b···O1 2.45(4) Å) but at the expense of an unacceptably low data/parameter ratio. The maximum residual electron density is 0.25 e/Å^3, 0.75 Å from H11B.

Crystal data. $C_{16}H_{36}N^+{\cdot}C_6H_5O^-{\cdot}C_6H_6O$, M_w=429.67, colourless prism 0.49×0.42×0.39 mm^3, monoclinic *Cc* (No. 9), a=13.721(5), b=13.447(3), c=16.160(5) Å, β=114.60(3)°, U=2711(1) Å^3, T=100 K, Z=4, D_x=1.053 g cm^{-3}, λ=0.71069 Å, μ=0.064 mm^{-1}, Enraf-Nonius CAD4 diffractometer,[26] $2.23<\theta<27.44°$, 8873 measured reflections, 3211 independent, 2964 with $I>2\sigma(I)$. Structure solved by direct methods and refined by least-squares using Chebyshev weights on F_o^2 to R_1=0.061 [$I>2\sigma(I)$], wR_2 0.172 (all data), 284 parameters, S=1.13, residual electron density +0.251/−0.241 e/Å^3.

Crystallograpic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-184571. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam. ac.uk).

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