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COMPLEXES OF AROMATIC HYDROXY COMPOUNDS WITH AMMONIUM SALTS AND AMINES NOVEL HYDROGEN-BONDING NETWORKS.[1]

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Abstract

Aromatic hydroxy compounds react with alkyl ammonium hydroxides or amines in aqueous solution to give n:1 complexes, the aromatic portions of which are linked by multiple hydrogen bonds.

Quaternary ammonium phenoxides have been implicated as intermediates in a number of reactions including alkylation of phenols under phase transfer conditions (1, 2). Stable crystalline complexes of phenols with diquaternary ammonium salts have been prepared under aqueous alkaline conditions (3, 4) and were found to contain both phenolate ion and phenol. Formation of similar complex anions has been reported in the case of ammonium salts of halogenated and nitrated phenols (5, 6). Although considerable literature exists on phenol/amine and phenol/ammonium interactions, few products have actually been isolated and characterized. In the present communication, we describe a series of discrete n:1 complexes of phenols or catechol with ammonium salts or amines (see Table). Although ammonium phenolates or phenoxides have been routinely assigned 1:1 compositions in the literature all of our products have $n>2$.

We have found that addition of an aqueous solution of a tetraalkyl ammonium hydroxide to a stirred aqueous solution of phenol or catechol results in almost immediate precipitation of the complex (e.g. 1-6). Once the stoichiometry of the product is established excellent yields can be obtained by using the correct molar ratio of starting materials. In most cases the products can be purified by crystallization and are obtained as sharp-melting crystalline solids. Complexes (7,8) can also be obtained by reaction of 4-nitrophenol with tetramethyl ammonium hydroxide or by reaction of catechol with the betaine $Bu_3\overset{+}{N}CH{=}CHCO_2^-$ (cf 7). Similarly, reactions of catechol with tributylamine or dibutylamine yield crystalline 2:1 and 3:1 complexes (9, 10) respectively. In these cases the amine is added directly to the aqueous solution of aromatic hydroxy compound. The aromatic/ammonium ion stoichiometry, as indicated by ^1H n.m.r. analysis, varied from 2:1 (e.g. catechol/Bu_4NOH) to 5:1 (phenol/Me_4NOH).

The structures are held together by a complicated network in which the phenolate oxygen is involved in multiple hydrogen bonds. This has been illustrated in 1 and 5 by X-ray crystal structure analyses (8).

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Complexes of aromatic hydroxy compounds.

No.	Aromatic hydroxy compound	Ammonium salt or amine	Complex	Description	m.p. (°C)
1	Phenol	Me_4NOH	$[(C_6H_5OH)_4][C_6H_5O^-][Me_4N^+]$	Col. needles (W)	82-84.5
2	Phenol	Et_4NOH	$[(C_6H_5OH)_3][C_6H_5O^-][Et_4N^+]$	Oil	-
3	Phenol	$^nBu_4NOH$	$[(C_6H_5OH)_2][C_6H_5O^-][^nBu_4N^+]$	Col. solid	67-69
4	Catechol	Me_4NOH	$[(HOC_6H_4OH)_3]$ $[HOC_6H_4O^-][Me_4N^+]$	Light brown flakes (W)	136-138
5	Catechol	Et_4NOH	$[(HOC_6H_4OH)_2]$ $[HOC_6H_4O^-][Et_4N^+]$	Light brown needles (W)	84-86
6	Catechol	$^nBu_4NOH$	$[HOC_6H_4OH][HOC_6H_4O^-]$ $[^nBu_4N^+]$	Greenish needles (E/P)	131-133
7	4-Nitrophenol	Me_4NOH	$[O_2NC_6H_4OH]$ $[O_2NC_6H_4O^-][Me_4N^+]$	Yellow flakes (A/P)	179-181
8	Catechol	$^nBu_3\overset{+}{N}CH{=}CHCO_2^-$	$[HOC_6H_4OH][HOC_6H_4O^-]$ $[^nBu_3\overset{+}{N}CH{=}CHCO_2H]$	Col. needles (E/P)	108-109.5
9	Catechol	$^nBu_3N$	$[HOC_6H_4OH][HOC_6H_4O^-]$ $[^nBu_3\overset{+}{N}H]$	Col. needles (E/P)	93.5-95
10	Catechol	$^nBu_2NH$	$[(HOC_6H_4OH)_2]$ $[HOC_6H_4O^-][^nBu_2\overset{+}{N}H_2]$	Light brown needles (P)	85-87.5

Col. = colorless; A = acetone; E = EtOAc; P = petroleum ether (b.p. 60-80°C); W = water.

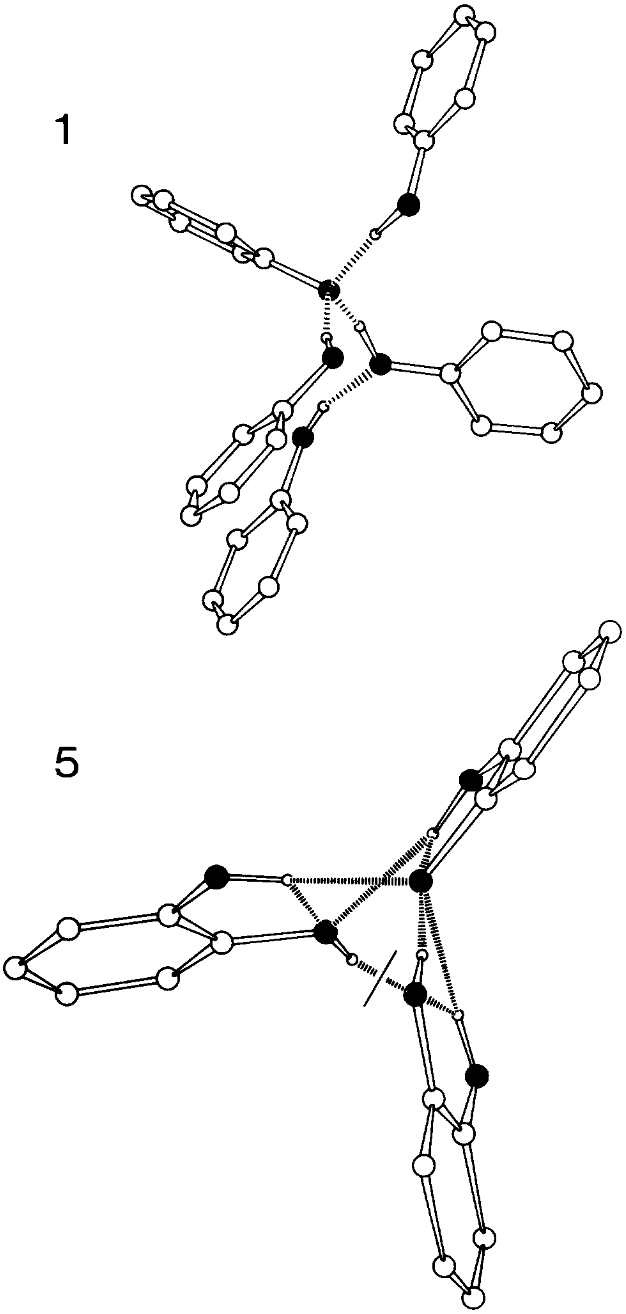
The first of the three catechol residues of compound 5 is a catecholate ion in which the charged oxygen is hydrogen-bonded intramolecularly to the _ortho_ hydroxyl, intermolecularly to both hydroxyl protons of the second catechol residue, and intermolecularly to a single hydroxyl of the third catechol residue. An additional hydrogen bond exists between the second and third rings. Thus the three aromatic rings are linked by four hydrogen bonds (Fig 1). Chains of these catechol triads are held together by further hydrogen bonding.

Compound 1 has a phenoxide oxygen which is likewise intermolecularly hydrogen-bonded to three different phenolic hydroxyls (9): the fifth aryl residue in this case is incorporated through hydrogen-bonding to the oxygen of one of these three phenolic hydroxyls (Fig. 1).

Steric constraints due to increasing cation size limit the number of aromatic rings involved in a complex. In addition the increased opportunities for hydrogen-bonding offered by the extra hydroxyl groups in the catechol complexes consistently result in one less aryl residue being present than in the phenol analogue. A different situation exists in the case of 7 due to the presence of the nitro group which can also hydrogen-bond.

The ^{13}C n.m.r. spectra of all compounds show aromatic resonances for only one type of ring (10). Similarly, the ^1H n.m.r. spectra of the catechol complexes show symmetrical multiplets in the aromatic region for AA^1BB^1 systems. The equivalence of these signals and averaging of the chemical shifts indicate very rapid exchange by intra- and intermolecular proton transfer between ionized and unionized catechol. Rapid and complete exchange of the phenolic hydroxyl hydrogens with the deuterium of $CDCl_3$ suggests possible application of some complexes in the preparation of deuterium labelled compounds.

Figure 1. Hydrogen-bonding networks of complexes.



In 5 view is along the direction of the chain of catechol triads. The hydrogen-bond interrupted by a solid line is between molecules in adjacent triads.

The coupling constant $^1J_{CH}$ for $\overset{+}{N}\text{-}CH_3$ or $\overset{+}{N}\text{-}CH_2$ carbons in **1-8** is in the range 142-145 Hz (the corresponding coupling in $Bu_3\overset{+}{N}CH{=}CHC\overset{-}{O_2}$ is 144 H_z); in the less-substituted **9** and **10** the values are 132 and 134 Hz respectively. A characteristically high $^1J_{CH}$(~194 Hz) is observed for the olefinic carbon bonded to the nitrogen in the $Bu_3\overset{+}{N}CH{=}CHCO_2H$ ion of complex **8** (cf 11). The analogous coupling in $Bu_3\overset{+}{N}CH{=}CHC\overset{-}{O_2}$ is 192.2 Hz. In all symmetrically substituted tetraalkyl ammonium complexes we also observed carbon-13/nitrogen-14 coupling in the signal for the methyl ($^1J_{CN}$ 4.0-4.1 Hz) or methylene ($^1J_{CN}$ 2.3-3.4 Hz) carbon bonded to nitrogen. Coupling between the methyl hydrogens and nitrogen ($^3J_{NH}$ ~ 2.5 Hz) in the tetraethyl ammonium complexes **2** and **5** was also observed in their ^1H n.m.r. spectra.

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