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SYNTHESIS AND SOLVATOCHROMIC AND ACID–BASE REACTIONS OF A BETAINE AND SALTS OF 4-N-PYRIDINIUMCATECHOL

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Oxidation of catechol by phenyliodosyldiacetate in the presence of pyridine gives 4-N-pyridiniumcatechol salts whose structures are confirmed by an independent synthesis from 2,2-dimethyl-5-aminobenzodioxole. The spectroscopically determined ionization constants for the 4-N-pyridiniumcatechol cation depend on the nature of the buffer cation solution (sodium, ammonium, tetraethylammonium). The large solvatochromic shift in the long wavelength absorption band of the betaine of 4-N-pyridinium-catechol followed the empirical scale of solvent polarity E_T^N. *Introduction of the N-pyridinium group in position 4 increases the acidity of the catechol by 2.7 pK units, which is an almost identical effect to the introduction of a 4-nitro group. However, the solvatochromism for the anion of 4-nitrocatechol is insignificant. The compounds were characterized by their* ^1H *NMR and IR spectra.*

Betaines of N-pyridinium phenols (4-N-pyridiniumphenolates) are curious compounds because of their very marked solvatochromism, thermochromism, and halochromism. These compounds have been studied from the sixties [1] to the present day [2-6]. 2-N-Pyridiniumphenolates have also been synthesized [7, 8]. Betaines of N-pyridinium bis atomic phenols have been repeatedly mentioned in the literature but not investigated. Nonetheless, such compounds are of considerable interest from the viewpoint of their color, solvatochromism, redox properties, and complex formation.

We are concerned here with the synthesis and study of the properties of 4-N-pyridiniumcatechols. G. Orteleva [9] first reported the synthesis of the iodide in 1902 by reaction of catechol with iodine in the presence of pyridine with the object of carrying out the addition of o-benzoquinone to pyridine. The structure of the reaction product was not definitely established. Later, E. Barnett and coworkers [10] treated catechol with bromine in the presence of pyridine and obtained N-pyridinium-catechol bromide but the position of the pyridine substituent (3 or 4) was not proven. Treatment of the bromide with aqueous ammonia gave a yellow-orange compound which was taken to be a betaine. Recently the Indian chemists J. Saxena and coworkers [11, 12] have repeated the reaction of catechol with pyridine and other heterocycles in the presence of iodine and bromine. ^{1}H NMR was used in [12] to provide evidence that the pyridinium residue added to position 4 and not to position 3 as claimed in their previous work [11].

To obtain 4-N-pyridiniumcatechol salts with strictly determined structures we selected the known synthetic route for N-arylpyridinium salts from arylamines and N-(2,4-dinitrophenyl)pyridinium chloride [13]. As starting arylamine we used a 4-aminocatechol with substituted hydroxyl groups, viz. 5-amino-2,2-dimethylbenzodioxole. Nitration of 2,2-dimethylbenzodioxole gives 2,2-dimethyl-5-nitrobenzodioxole [14, 15]. Catalytic hydrogenation [15] then gave 2,2-dimethylbenzodioxole-5-ammonium bisulfate (I). Reaction of the bisulfate I with N-(2,4-dinitrophenyl)pyridinium chloride in DMF solution in the presence of triethylamine gave 2,2-dimethyl-5-(N-pyridinium)benzodioxole perchlorate (II) in about 30% yield. The protecting group was readily removed by heating the perchlorate with concentrated hydrobromic acid and recrystallization of the 4-N-pyridiniumcatechol bromide (IIIc).

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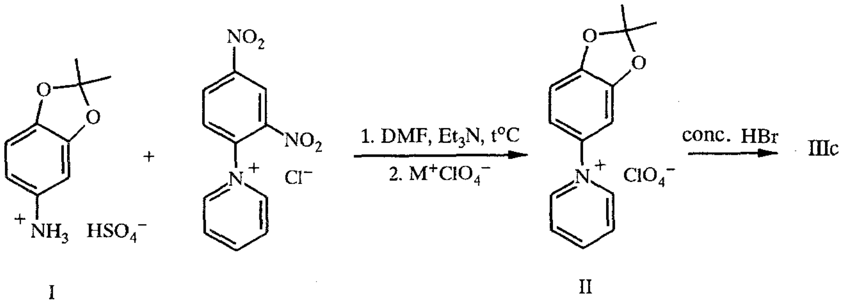
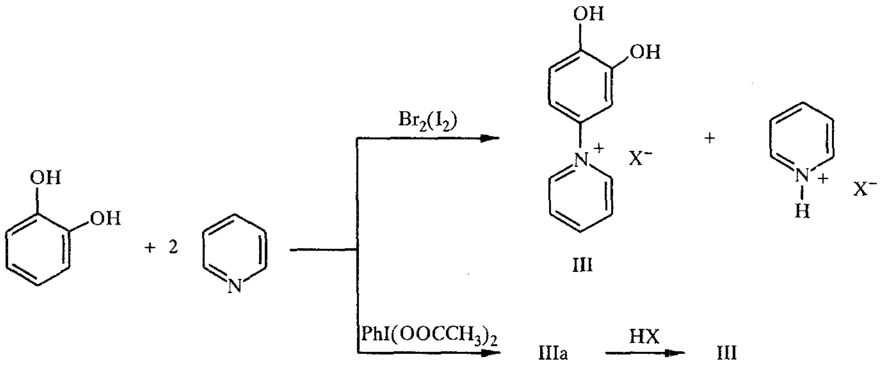


After obtaining the known compounds, the target salts of 4-N-pyridiniumcatechol were prepared by reaction of catechol with oxidants in the presence of pyridine. The use of bromine [10, 12] or iodine [9, 11] gave the bromide or iodide of 4-N-pyridiniumcatechol in an average yield of 35%. The ^1H NMR spectra (Table 1) of the bromides obtained by the two routes were identical.

We have shown that phenyliodosyl compounds are effective and promising oxidants of catechol for effecting the addition of pyridine or other heterocycles. The oxidation of catechol and several of its alkyl derivatives to o-benzoquinones by phenyliodosyldiacetate was first reported by A. Balaban [16]. We have carried out oxidation of catechol in the presence of pyridine using various phenyliodosyl compounds and proposed phenyliodosyldiacetate for the synthetic target. Phenyliodosyl compounds are two electron oxidants and are used in strictly equimolar amounts. In contrast to the reaction of catechol in the presence of bromine or iodine (where excess pyridine is used) the reaction with the diacetate can use equimolar pyridine, maximum yield being achieved with a two fold excess.



a X = CH3COOH; b X = Cl; c X = Br; d X = I; e X = ClO4

For the diacetate oxidation the product is separated by addition of HCl and acetone as the chloride (IIIb) since it is almost insoluble in acetone. The yield of IIIb is 60% (based on catechol). Perchlorate IIIe can be precipitated from aqueous solutions of the chloride or bromide using $HClO_4$ or $NaClO_4$ solutions.

The betaine of 4-N-pyridiniumcatechol (4-N-pyridiniumcatecholate, IV) is precipitated from aqueous solutions of salts III (excluding the perchlorate IIIe) using an aqueous solution of ammonia to give orange-yellow, long, fine, interlocking needles. Treatment of the perchlorate IIIe with aqueous sodium carbonate or aqueous ammonia give not betaine IV but the less soluble dimer salt (4-N-pyridiniumcatecholate-4-N-pyridiniumcatechol, V) as yellow, shining leaflets. We believe the dimer V is formed because of O...H...O hydrogen bridging. Thus in their IR spectra in the region 3500-2500 cm^{-1} perchlorate IIIe shows a maximum near 3370 cm^{-1} and this is shifted to 3000-3100 cm^{-1} and markedly broadened in V.

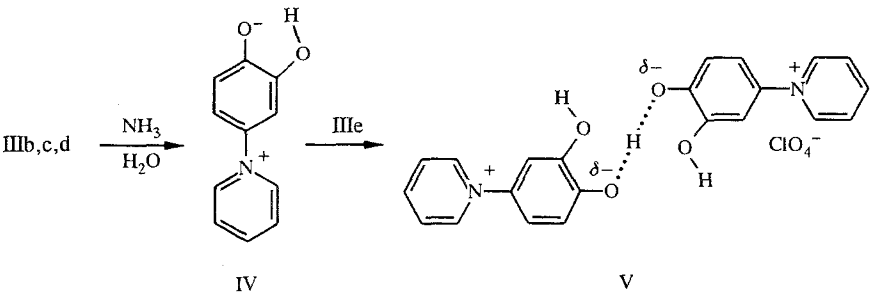


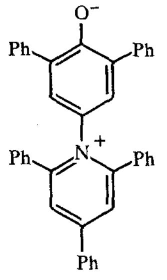
TABLE 1. ^{1}H NMR spectra of Catechol Derivatives

Compound	Catechol ring protons in positions			Pyridinium ring protons in positions			Other protons
	3	5	6	2',6'	3',5'	4'	
I	6,73...6,35 (m 3H)						1,52 (6H, s, CH_3), 5,7 (br , NH_3^+)
II	7,41 (1H, d)	7,31...7,04 (2H, m)		9,17 (d,2H)	8,18 (t, 2H)	8,66 (t, 1H)	1,69 (6H, s, CH_3)
IIIb	7,16 (1H, m)	7,01 (2H, m)		9,15 (d,2H)	8,16 (t, 2H)	8,63 (t, 1H)	10,02 (1H, s, OH), 9,88 (1H, s, OH)
IIIc	7,15 (1H, s)	7,05...6,88 (2H,m)		9,15 (d,2H)	8,16 (t, 2H)	8,63 (t, 1H)	9,8 (2H, br , OH)
IIId	7,13 (1H, s)	7,05...6,88 (2H,m)		9,14 (d,2H)	8,16 (t, 2H)	8,64 (t, 1H)	9,86 (1H, s, OH), 9,72 (1H, s, OH)
IIIe	7,17 (1H, s)	7,1...6,94 (2H,m)		9,2 (d,2H)	8,22 (t, 2H)	8,68 (t, 1H)	9,8 (2H, br ., OH)
IV IV·$2H_2O$	6,66...6,48 (2H, m)		6,29 (1H,d)	8,98 (d 2H)	7,97 (t, 2H)	8,37 (t, 1H)	
VIII	7,43 (1H, d)	7,75 (1H, m)	6,31 (1H, d)				0,95 (d 12H, CH_3), 1,2...1,7 (m, 16H, CH_2), 3,0 (t, 8H, CH_2N)

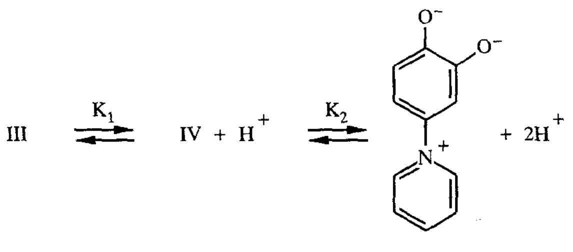
Perchlorate V is also precipitated when aqueous solutions of betaine IV and perchlorate IIIe are mixed.

Betaine IV is a dihydrate, moderately soluble in water, less in ethanol, DMF, pyridine, and acetonitrile, and insoluble in chloroform, benzene, acetone, and ether. The compound is stable on storage; in a vacuum desiccator it loses water and turns red [10]. In moist air it again becomes orange-yellow. On heating above 80°C it gradually darkens and at 100°C and above a red-brown, i.e., it undergoes irreversible change. The material does not have a clear melting point, the temperature of decomposition depending on the rate of heating.

Betaine IV is clearly solvatochromic. A solution in water is yellow, in ethanol orange, in DMF dark red, and in pyridine violet. The long wavelength absorption maxima for IV in different solvents are given in Table 2 together with the maxima for the analogous betaine 4-N-(2,4,6-triphenylpyridinium)-2,6-diphenylphenolate VI as reported by Ch. Reichardt [1, 2, 6].



VI



VII

A good correlation is seen between the solvent polarity constant E_T^N [2] and the energy of the long wavelength absorption (with the exception of an aqueous solution). The difference (hypsochromic shift) of the long wavelength absorption energies for IV and VI amount to 0.51 to 0.58 eV (Fig. 1).

The long wavelength absorption of such phenolate betaines is basically due to the so-called intramolecular charge transfer (ICT) with light since the molecule consists of two parts opposite in polarity and electronic properties, viz. an electron donating anion and electron accepting cation. The highest occupied molecular orbital (HOMO) is basically localized on the anionic phenolate and the lowest unoccupied molecular orbital (LUMO) on the cationic pyridinium hence excitation irradiation causes transfer of electronic charge from one part of the molecule to the other and the first excited state differs significantly in polarity from the ground state. If the ground state has bipolar character (betainoid) and has a large dipole moment, the first excited state (through ICT) is characterized by a much decreased dipole moment or even one of opposite sign. This phenomenon has a considerable effect on the solvation of the ground and excited states and this is the basis of the solvatochromism. The energy of the ICT depends on the donor – acceptor properties of the parts of the bipolar betaine molecule [7]. Hence increasing the electron acceptor properties of one part causes a bathochromic shift. Such a shift can be observed, for example, in changing

TABLE 2. Long Wavelength Absorption Maxima for Betaine 4-N-Pyridiniumcatechol (IV) and Betaine 4-N-(2,4,6-Triphenylpyridinium)-2,6-diphenylphenol (VI) in Different Solvents

Solvent	Solvent constant E_T^N [2]	Long wavelength absorption maximum in nm and eV				Difference in energy for maximum absorption, eV
		Betaine of 4-N-pyridinium-catechol (IV)		Betaine of 4-N-(2,4,6-triphenylpyridinium)-2,6-diphenylphenol (VI) [1]		
Water	1,000	398	3,11	453	2,74	0,37
Methanol	0,765	418	2,96	515	2,41	0,55
Ethanol (abs.)	0,654	445	2,78	551	2,25	0,53
2-Propanol	0,552	465	2,66	588	2,11	0,55
Acetonitrile	0,472	495	2,50	622	1,99	0,51
DMF	0,404	500	2,48	653	1,90	0,58
Pyridine	0,293	535	2,31	710	1,75	0,56

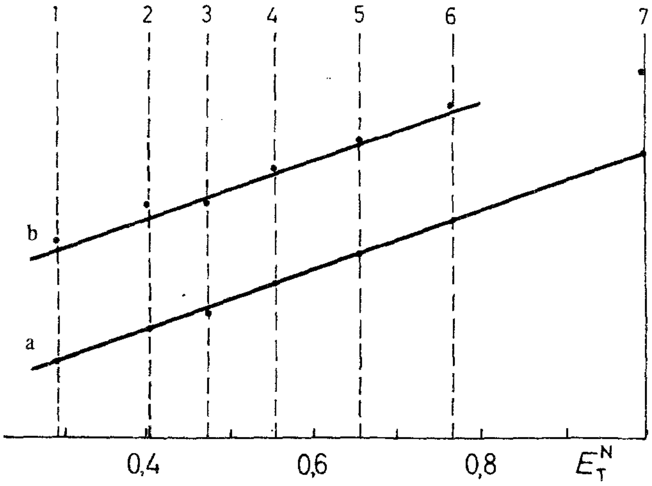


Fig. 1. Relationship between the energy of the long wavelength absorption hν and the solvent polarity constant E_T^N [2] for 4-N-(2,4,6-triphenylpyridinium)-2,6-diphenylphenolate (VI) (curve a) and betaine IV (curve b) in the following solvents: pyridine (1), DMF (2), acetonitrile (3), 2-propanol (4), abs. ethanol (5), methanol (6), and water (7).

from an N-pyridinium to a 2,4,6-triphenyl-N-pyridinium substituent and even more strongly for N-quinolinium. An increase in the donor properties of the anionic part also causes a bathochromic shift, for example in changing from unsubstituted phenol to 2,6-dialkyl and 2,6-diphenyl phenols [1]. Hence it is not surprising that the yellow-orange colored solution of betaine IV changes to a red colored betaine anion (VII) at pH greater than 12 (Table 3, Fig. 2).

In order to determine the first and second ionization constants for 4-N-pyridiniumcatechol we have studied its spectral absorption in aqueous solutions at different pH. Fig. 2 shows the typical spectral absorption changes at increased pH. Formation of the betaine gives rise to absorption in the region 350-400 nm. It should be noted that the absorption maxima for IV at the same pH can vary with the composition of the buffer solution and, in fact, the nature of the cation. For sodium ions the maximum absorption is observed at 362 nm but for solutions of ammonium salts it is at 390 nm (see Table 3). use of tetraethylammonium salts leads to a further small bathochromic shift to 398 nm. We feel that this si due to a reaction of sodium or ammonium ions with oxygen atoms of betaine IV (halochromism [5]). The intrinsic spectrum of the betaine is only observed in the absence of complex forming cations. This also affects the ionization constants K_I (see Table 3), the constant for the sodium ion being almost an order of magnitude less than that for tetraethylammonium ions.

In alkaline pH greater than 12 the absorption at 460-470 nm characterized the betaine anion (VII) and the effect of the buffer composition on the absorption maximum was very markedly less. A peculiar effect was noted when measuring at pH around 10-12. At a concentration of 10^{-4} mole·liter^{-1} it was not possible to obtain a set of spectral curves with a good isosbestic point and this may point to the occurrence in the equilibrium IV $\rightleftarrows$ VII + H^+ of a third component. Only at a

TABLE 3. Ionization Constants for 4-N-pyridiniumcatechol Salts and Electronic Absorption Spectra of the Betaine and Betaine Anion of 4-N-Pyridiumcatechol in Different Aqueous Buffers

Buffer solution	Electronic absorption spectrum, λ_{max}, nm (ε), c = 10^{-4} mole·liter^{-1} betaine (pH 9 to 10)	betaine anion (pH > 13)	pK_1 (±0,05)	pK_2 (±0,05)
Sodium hydroxide, sodium hydrogen phosphate, acetic acid	362 (4400) 265(8000)	462(4240) 295(7700) 250(8600)	8,05	11,80
Aqueous ammonia, ammonium chloride	390 (4150) 276 (7900) 242(12000)		7,85	
Tetraethylammonium hydroxide, phosphoric acid, acetic acid	398 (3650) 278 (6800) 242(9000)	468(4200) 297(7600) 252(8700)	7,15	12,25
	pH 11,1 420(4000) 286(8000) 244(7900)			
	pH 11.1 c = 10^{-5} mole·liter^{-1} 410...420(3150) 282(7000)			11,55

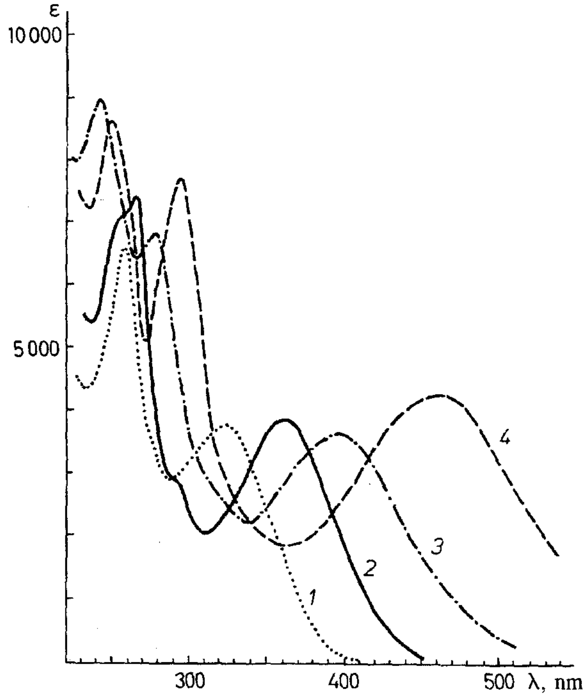


Fig. 2. Electronic absorption spectra of the associated and dissociated forms of 4-N-pyridiniumcatechol salts in aqueous solution: 1) perchlorate, solution pH less than 5; 2) betaine, pH 9-10, buffer solution sodium acetate-acetic acid; 3) betaine, pH 9-10, buffer tetraethyl-ammonium hydroxide–acetic acid–phosphoric acid; 4) betaine anion, pH greater than 13, sodium hydroxide solution.

concentration of 10^{-5} mole·liter^{-1} could we obtain an acceptable set of curves for calculation of K_2 (see Table 3). It should be noted that the above applies only to triethylammonium and not sodium buffer solutions. The obtained constant K_2 differs little with variation in buffer solution. We believe that ionization of betaine IV in the pH range where the concentrations of

IV and the anion VII are close is accompanied by dimerization via hydrogen bridging. This dimer IV·VII apparently has a dissociation constant less than 10^{-4} and dissociates completely only at 10^{-5} concentration. The presence of sodium ions hinders formation of such a dimer probably because of the strong interaction of sodium ions both with betaine IV and the anion VII.

The acidity of the 4-N-pyridiniumcatechol salts is comparable with the acidity of 4-nitrocatechol, for which $pK_1 = 7.00$ and $pK_2 = 11.25$ in aqueous solutions at 20°C (determined by potentiometric titration) [17]. Hence the electron acceptor effects of the nitro and N-pyridinium groups are very similar, increasing the acidity by 2.7 pK units with introduction of the 4-N-pyridinium group and 2.85 units with the 4-nitro group. It was interesting further to check what solvatochromic shift might occur for the 4-nitrocatechol anion. For this reason we synthesized tetrabutylammonium 4-nitrocatecholate (VIII) which is soluble in organic solvents. It was found that a change from aqueous solution to solution in chloroform caused the long wavelength absorption maximum to undergo only a small bathochromic shift (427 nm, $\varepsilon = 8300$ in water and 437 nm, $\varepsilon = 4800$ in chloroform).

Our experiments have shown that the N-pyridinium substituent plays an unusual role in producing a molecule with very high solvatochromism and that the betaine of 4-N-pyridiniumcatechol is of considerable interest in obtaining deeply colored metal complexes in nonaqueous solutions.

EXPERIMENTAL

^1H NMR Spectra were recorded on a Tesla BS 487C instrument with DMSO-d_6 solvent. IR Spectra were taken on a Specord IR-75 instrument in paraffin oil (1900 to 650 cm^{-1}) and hexachlorobutadiene (3600 to 2300 cm^{-1}). Electronic absorption spectra were recorded on a Specord UV-vis. Ionization constants were measured spectrophotometrically according to the method in [18].

The experimental work was carried out with the help of M. Ya. Dzelme and L. L. Paulin'sh.

2,2-Dimethylbenzodioxolyl-5-ammonium Bisulfate ($C_9H_{13}NO_6$, I). 2,2-Dimethyl-5-nitrobenzodioxole [14, 15] (1.95 g) was dissolved with heatin gin isopropanol (100 ml) and hydrogenated in the presence of Pd/$BaSO_4$ catalyst. After separation of catalyst, the product was evaporated to a volume of 20-30 ml and concentrated sulfuric acid (0.6 ml) was added with vigorous stirring. The yield of the colorless salt was 2 g (75%). On storage, the product gradually darkened.

2,2-Dimethyl-5-(N-pyridinium)benzodioxole Perchlorate ($C_{14}H_{14}ClNO_6$, II). N-(2,4-dinitrophenyl)pyridinium chloride (1.4 g, 5 mmole) and I bisulfate (1.3 g, 5 mmole) in DMF (10 ml) heated to 100°C, triethylamine (0.7 ml, 5 mmole) was added, and the heating was continued at 130-140°C for a further 45 min. The dark red colored solution changed to orange-brown. The solution was cooled and diluted with water (50 ml) and the liquid separated from a dark oil. The liquid was treated with activated carbon, filtered, and evaporated in vacuo. The residue was dissolved in water (10 ml), activated carbon added, and sodium perchlorate added to the filtrate. The product was held at 0 to 5°C for a day and the crystals separated and recrystallized from water (20 ml) with the addition of activated carbon (and sodium perchlorate to the filtrate). The yield was 0.5 g (30%) with mp 180-183°C.

4-N-Pyridiniumcatechol Bromide ($C_{11}H_{10}BrNO_2$, IIIc). A. perchlorate II (0.4 g) and conc. hydrobromic acid (10 ml) were heated to reflux and left in the refrigerator for 1 day. The yellow crystals were filtered and washed with acetone to give 0.3 g of product (91%) with mp 267-268°C (decomp.).

B. A mixture of bromine (10 ml, 0.2 mole) and pyridine (32 ml, 0.4 ml) was added to a solution of catechol (22 g, 0.2 mole) in methanol (60 ml) with cooling to 0-5°C and stirring. The crystalline product was filtered and recrystallized from a mixture of conc. hydrobromic acid and water (1:1) to give light yellow crystals (15 g, 34%) with mp 267-268°C (decomp.).

IR Spectrum: 3190, 3080, 1630, 1615, 1520, 1300, 1200, 935, 890, 835, 790 cm^{-1}.

4-N-Pyridiniumcatechol Iodide ($C_{11}H_{10}INO_2$, IIId). Catechol (11 g, 0.1 mole) was dissolved in a mixture of ethanol (10 ml) and pyridine (16 ml, 0.2 mole). Finely ground iodine (12.7 g, 0.05 mole) was added portionwise with stirring, regulating the speed of addition so that the temperature of the mixture did not exceed 5 to 10°C. Stirring was continued until all of the iodine had reacted. The mixture was allowed to stand for 2 days in the refrigerator and the crystalline product filtered and washed with ethanol to give 8.4 g of product. It was recrystallized from a mixture of ethanol and concentrated hydriodic acid (75 ml, 9:1 by volume). The yellow crystalline product (5.5 g, 35% based on iodine) had mp 243-245°C (decomp.).

IR Spectrum: 3265, 3165, 1628, 1606, 1520, 1292, 1192, 912, 862, 812, 772 cm^{-1}.

4-N-Pyridiniumcatechol Chloride ($C_{11}H_{10}ClNO_2$, IIIb). Catechol (1.1 g, 10 mmole) in methanol (10 ml) was treated with pyridine (1.6 ml, 20 mmole) with cooling to 6-8°C and phenyliodosyldiacetate (3.3 g, 10.25 mmole) added with stirring.

After solution of the material a solution of concentrated sulfuric acid (3 ml) in acetone (50 ml) was added. The mixture was held at 2-4°C for several hours and the chloride filtered off as slightly brown crystals. Washing with acetone gave product (1.35 g, 60% based on catechol) with mp 270-272°C (decomp.). The chloride was recrystallized from dilute hydrochloric acid (1:1).

IR Spectrum: 3120, 2970, 1630, 1608, 1520, 1294, 1212, 1122, 916, 878, 818, 778 cm^{-1}.

4-N-(pyridiniumcatechol) Perchlorate ($C_{11}H_{10}ClNO_6$, IIIe). Chloride IIIb (0.22 g) was dissolved in water (5 ml) with heating. $HClO_4$ (0.5 ml, 55%) was added and the product left to give yellow crystals (0.22 g, 75%) with mp 240-242°C (decomp.).

IR Spectrum: 3368, 3132, 1634, 1618, 1526, 1300, 1196, 1120, 1050, 914, 862, 776 cm^{-1}.

4-N-Pyridiniumcatechol-4-N-pyridiniumcatecholate Perchlorate ($C_{22}H_{19}ClN_2O_8$, V). Perchlorate IIIe (0.575 g, 2 mmole) was dissolved with heating in water (50 ml) and a solution of sodium carbonate (0.21 g, 2 mmole) in water (10 ml) added. On the following day the product was filtered to give a yellow finely crystalline powder. Crystallization from water (80 ml) and holding in a refrigerator gave yellow, shining leaflets (0.25 g).

IR Spectrum: 3124, 3076, 1630, 1505, 1290, 1198, 1095, 922, 866, 822, 778 cm^{-1}.

Betaine of 4-N-pyridiniumcatechol Dihydrate ($C_{11}H_9NO_2 \cdot 2H_2O$, IV·$2H_2O$). Chloride IIIb (1.1 g) was dissolved in water (10 ml), heated, and concentrated aqueous ammonia (0.7 ml) added. The mixture was held at 2-4°C for a day and the yellow-orange crystals formed filtered off, washed with water and acetone, and dried at room temperature to give the betain (1 g, 90%). Crystallization from water (15 ml) gave long, fine, yellow-orange, interlocking needles (0.9 g).

IR Spectrum: 3120 (broad), 1646, 1630, 1582, 1510, 1282, 1132, 1124, 916, 850, 778 cm^{-1}.

Tetrabutylammonium 4-nitrocatecholate Hydrate ($C_{22}H_{40}N_2O_4 \cdot H_2O$, VIII·$H_2O$). 4-Nitrocatechol (0.6 g, 3.87 mmole) was obtained by hydrolysis of 2,2-dimethyl-5-nitrobenzodioxole [14, 15] by heating in concentrated hydrobromic acid. It was dissolved in water (40 ml) and a 10% aqueous solution of tetrabutylammonium hydroxide (10 g, 3.87 mmole) added. The yellow precipitate was filtered, washed with water, and dried at room temperature to give product (1.45 g, 94%) with mp 122-125°C. It can be recrystallized by dissolving in chloroform and diluting with benzene.

IR Spectrum: 3460, 3360, 2960, 2872, 1662, 1608, 1534, 1494, 1418, 1338, 1274, 1246, 1222, 1182, 1118, 1078, 946, 876, 820, 734 cm^{-1}.

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