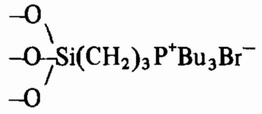
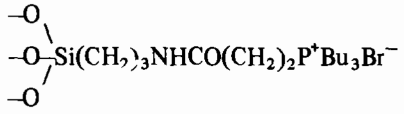
phosphonium salts supported on silica gel (*1, 2, 3* and *4*)



$(-O)_3Si(CH_2)_3P^+Bu_3Br^-$

1

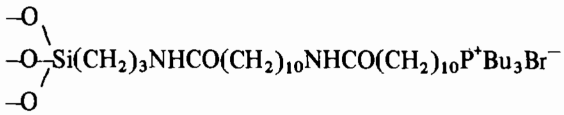


$(-O)_3Si(CH_2)_3NHCO(CH_2)_2P^+Bu_3Br^-$

2

$(-O)_3Si(CH_2)_3NHCO(CH_2)_{10}P^+Bu_3Br^-$

3



$(-O)_3Si(CH_2)_3NHCO(CH_2)_{10}NHCO(CH_2)_{10}P^+Bu_3Br^-$

4

are different from those immobilized on polystyrene matrices because the catalyzed reaction occurs on the adsorbed substrate and in a microenvironment constituted by the water present on the inorganic matrix.

Kinetic measurements on the reaction:

$$RX + KI \xrightarrow[\text{with or without stirring}]{\text{cat., water}} RI + KX$$

are carried out. The accessibility of both organic and inorganic phase on such a system is facilitated by the peculiar structure of the silica gel functionalized phosphonium salts: the silica skeleton and the covering organic functions are permeable to both organic and aqueous phase.

Nevetheless the anions exchange in the inner catalytic centers, without stirring, is the more difficult process. Our results (by Arrhenius plots, kinetics without or with different stirring speed, *etc.*) well agree with a mechanism in which only a molar ratio (function of stirring speed and of the alkyl chain in the catalyst) of the catalytic centers catalyze full time the reaction; all the remainder is equal to the mechanism of the soluble onium salts.

Because such systems are constituted by a polar domain (silica gel and onium salt) and by a hydrophobic one (organic chain), and, moreover, work *via* substrate adsorption, they are able to catalyse the reaction carried out in water, as the micelles do. In the decarboxylation of 6-nitrobenzixazole-3-carboxylate (test reaction for micellar catalysis) *catalytic* amounts of *3* (0.05 molar equiv. with respect to the carboxylate) give 2-cyano-5-nitrophenolate with a $k_{dec} = 1.1 \times 10^{-4}\ s^{-1}$ in water at 30 °C; this value is higher or comparable with the other micellar agents as the cationic polysoaps [4] and the polycrown ethers [5].

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Complexing Properties of Phenol–Formaldehyde Cyclic Oligomers and Their Derivatives

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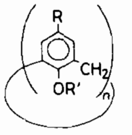
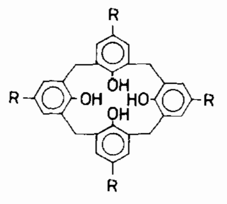
Cyclic oligomers (I, R′ = H) obtained from the base-catalyzed reaction of *p*-substituted phenols and formaldehyde are an old class of compounds [1] which are experiencing new interest because of their



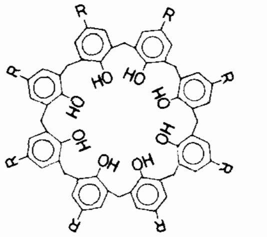
I

cone-shape that brought them the name of *calixarenes* [2]. The tetramer (II) we isolated from the reaction of *p*-t-butylphenol and formaldehyde forms a stable 1:1 chlatrate of cage-type with toluene which is held into the cavity as guest [3]. Chlatrates, whose structures are under investigation, are also formed by the octamer (III) which has been isolated from the same reaction mixture.



II

R= C(CH$_3$)$_3$



III

Both compounds have been used as *ordered building blocks* for open chain cation ligands [4] obtained by alkylation of the phenolic OH with different binding groups [I, $R' = CH_3, CH_3CO–, –(CH_2CH_2O)_n\text{-}CH_3$].

The alkylation of II and III destroys the cup-like structure of the starting compounds, which is mainly determined by intramolecular hydrogen bonds, giving products with different geometries and complexing abilities toward cations. Derivatives of the tetrameric oligomer (II) are a mixture of stereoisomers which do not interconvert at ambient temperature and have non convergent binding groups. Their complexation toward Li^+, Na^+, K^+, NH_4^+, $[C(NH_2)_3]^+$ picrates is very poor, these salts being not extracted by the ligands from water to $CDCl_3$ and CH_2Cl_2.

Derivatives of the octamer (III) have chains which easily pass through the central hole and are able to wrap the cations as the *octopus* molecules [4]. Methyl and acetyl derivatives of III do not complex any tested cation, while compounds with even short poliethers chains [I, $R' = –CH_2CH_2OCH_3$, $–(CH_2\text{-}CH_2O)_2CH_3$] are able to extract picrates from water to CH_2Cl_2 and $CDCl_3$.

A remarkable strong complexation of the latter compounds is observed toward guanidinium cation whose tetraphenylborate is dissolved in CDCl3 up to a ratio [salt]/[ligand] = 1.3–1.5 and picrate extracted from H_2O to CH_2Cl_2 with an extraction constant $K_e \simeq 2 \times 10^4\ M^{-2}$.

Results obtained with other ligands built on cyclic oligomers derived from *p*-cresol and *p*-octylphenol will be also reported.

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Solvent Effects upon Dielectric, Spectroscopic and Thermodynamical Manifestations of EDA Interaction between Iodine and Pyridines

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Dipole moments and the contributions of the dative structure (F_N) in the ground state of pyridine and γ-picoline complexes with I_2 in non-polar and weakly polar solvents were determined. The results thus obtained were compared with those arising from the solvent effect on the spectroscopic behaviour of the amine–I_2 adducts. Correlations were found between the solvent induced enhancement of the dative structure contribution determined from dipole moment measurements and calculated from the force constants of ν(I–I) and ν(N–I) vibrations. A similar correlation of F_N was found with respect to the solvent shift of the transition energy ${}^3\pi_{ou^+} \leftarrow {}^1\Sigma_{g^+}$ in the I_2 molecule bounded to amines. Solvent effects were also discussed using formation enthalpies ΔH_{AD} for pyridine–I_2 complex on the basis of the thermodynamic cycle. The dependence of F_N and complex stability upon the solvation type were analysed in terms of the Onsager reaction field theory and also through correlations with empirical parameters of solvent activities, such as k_M and E_T.

Solution Chemistry of $[PNP]^+$-Salts in Water and Methanol

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The $[PNP]^+$-cation [1] has been shown to be a valuable alternative to the usually employed onium cations for studies of anions in alcohols and various aprotic solvents [2].

$[PNP]^+Cl^-$, which serves as the starting material, is simple to synthesize in high yield and is fairly cheap. Due to the considerable solubility of this salt in warm water, other salts can be easily prepared by precipitation. These salts are generally easy to purify, are very soluble in most alcohols and dipolar aprotic solvents and are non-hygroscopic.