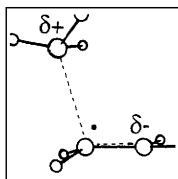


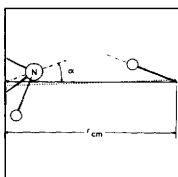
# Chemical Society Reviews

Volume 22 Issue 3 Pages 143-212 June 1993



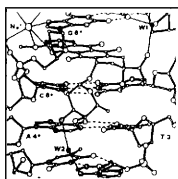
**CENTENARY LECTURE. The Pursuit of Selectivity in Radical Reactions** By Athelstan L. J. Beckwith (pp. 143-151)

The recognition of the factors which influence the chemo-, regio-, and stereo-selectivity of organic free radical reactions has underpinned recent developments in the application of such reactions to the synthesis of complex molecules. In this review the role of thermochemical, stereoelectronic, steric, and polar effects in determining selectivity will be discussed and illustrated with examples drawn mainly from recent work carried out at the Australian National University.



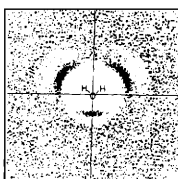
**The Nature of Ammonium and Methylammonium Halides in the Vapour Phase: Hydrogen Bonding versus Proton Transfer** By A. C. Legon (pp. 153-163)

The familiar white smoke, so redolent of school chemistry, is the ultimate product when ammonia and hydrogen chloride gases mix but what is the nature of the heterodimer first formed? Is it the simple hydrogen-bonded species  $\text{H}_3\text{N} \cdots \text{HCl}$  or is the proton transferred to give the ion pair  $\text{H}_3\text{NH}^+ \cdots \text{Cl}^-$ ? How is the extent of proton transfer affected by progressive methylation of  $\text{NH}_3$ , by replacement of Cl with Br and then I, and by substitution of N by P? Recent advances in the rotational spectroscopy of supersonically expanded jets have led to answers to these fundamental questions.



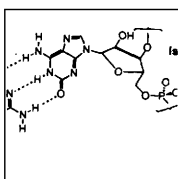
**Discovery and Development of Anthracycline Antitumour Antibiotics** By J. William Lown (pp. 165-176)

The armamentarium of the oncologist includes 40-50 clinically useful chemical agents. The paradigm of cytotoxic anticancer agents is doxorubicin, an anthracycline, which is amongst the most widely prescribed and effective of anticancer agents. This review attempts to summarize the discovery and development of the anthracyclines, their classification on the basis of structure and mechanism, and evidence on their several modes of action. Recent identification of cellular targets including topoisomerases and helicases present new challenges to the synthetic chemist and pharmacologist.



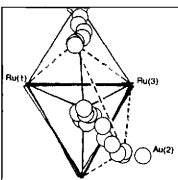
**Computer Simulations on Aqueous Solutions of Some Non-Electrolytes** By Koichiro Nakanishi (pp. 177-182)

The structure of aqueous solutions of non-electrolyte amphiphiles is often of complex nature and methods to investigate the solution structure experimentally are limited. Recent development of molecular simulation (Monte Carlo and molecular dynamics calculations) has made it possible to examine the structure and dynamics at the molecular level. Three representative cases, 2-methyl-propan-2-ol, urea, and acetonitrile, are described.



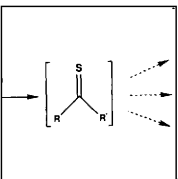
**Biosynthetic Incorporation of Non-natural Amino Acids into Proteins** By Josef Brunner (pp. 183-189)

This article summarizes recently developed methods of incorporating non-natural amino acids into proteins. These methods rely on the chemical aminoacylation of artificial [(semi)synthetic or *in vitro* transcribed] transfer RNAs that recognize a unique 'blank' codon in appropriately engineered messenger RNAs. By introducing 'designer' amino acids, it is possible to generate novel probes of protein structure and function.



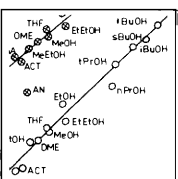
**Structural Systematics in Molecular Inorganic Chemistry** By A. Guy Orpen (pp. 191-197)

Applications of crystal structural data to molecular inorganic chemistry are described. The use of empirical correlations between structural parameters to provide insights into transition metal chemistry is illustrated. Examples are given of applications of this approach to determining typical molecular dimensions, testing theories of bonding, exploring conformational behaviour of flexible species, and analysing reaction pathways. The relationship between the experimental observations and the theory used in their interpretation is discussed.



**Some Recent Synthetic Routes to Thioketones and Thioaldehydes** By William M. McGregor and David C. Sherrington (pp. 199-204)

Thiocarbonyl compounds are reactive intermediates used to introduce sulfur heteroatoms into organic syntheses. Such species can either be synthesized and then further modified, or generated and reacted *in situ*. The crucial synthetic step in such syntheses is the generation of the inherently unstable C-S  $\pi$ -bond, thus creating a reactive 'handle'. This review explores the plethora of methods for the generation of both transient and stable thioaldehydes and thioketones.



**Electrolytes in Binary Solvents: An Experimental Approach** By S. Taniewska-Osińska (pp. 205-212)

The lack of an adequate theory to describe the properties of electrolytic solutions in binary mixed solvents makes research on such systems important. This article collates the standard enthalpies of salt solutions in water-organic solvents with the properties of solvent component mixtures, in order to discuss the effect of ions on solvent structure. Plots of  $\Delta H_s^0$  for electrolytes with and without organic ions are compared in several groups of mixed solvents. The  $\Delta H_s^0$  maxima for organic ions are described by means of hydrophobic effects parameters of organic co-solvents. The role of hydrophobic interactions is shown by the comparison of  $\Delta H_s^0$  plots in water-organic and organic-organic solvents.

## **Articles that will appear in forthcoming issues include**

Cholaphanes *et al.*; Steroids as Structural Components in Molecular Engineering **A. P. Davis**

The Physiological Role of Nitric Oxide **A. R. Butler and D. L. H. Williams**

The Lower Oxidation States of Indium **D. G. Tuck**

Interplay of Theory and Experiment in the Determination of Transition-state Structure **I. H. Williams**

Catalytic Antibodies: Mechanistic and Practical Considerations **J. D. Stewart and S. J. Benkovic**

Interactions of Metal Ions with Nucleotides and Nucleic Acids and their Constituents **H. Sigel**

Catalysis by Metal Ions in Reactions of Crown Ether Substrates **R. Cacciapaglia and L. Mandolini**

Thermodynamics of Solvation in Mixed Solvents **W. E. Waghorne**

The Chemistry of Cyclopropylmethyl and Related Radicals **D. C. Nonhebel**

Electrochemistry in Media of Low Dielectric Constant **A. Abbott**

Mechanisms of Solvolytic Alkene-forming Elimination Reactions **A. Thibblin**

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