$$\mathrm{RCOOH\cdots S + RCOOH\cdots S \rightleftharpoons RCOOH\cdots RCOOH\cdots S + S,}$$

$$\mathrm{RCOOH\cdots S + ROH\cdots S \rightleftharpoons RCOOH\cdots ROH\cdots S + S,}$$

$$\mathrm{ROH\cdots S + RCOOH\cdots S \rightleftharpoons ROH\cdots RCOOH\cdots S + S,}$$

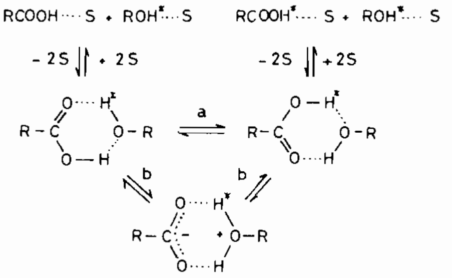
$$\mathrm{ROH\cdots S + ROH\cdots S \rightleftharpoons ROH\cdots ROH\cdots S + S.}$$

By comparison of these data with the thermodynamic data of proton donor dimerisation in other media linear enthalpy–entropy relationships are obtained which are typical for the functional proton donor group and which are useful for estimating the degree of specific solute–solvent interactions

$$\mathrm{AH\cdots S + S' \rightleftharpoons AH\cdots S' + S,}$$

where S, S′ = THF, benzene, CCl_4, cyclohexane.

The thermodynamic and kinetic data lead to the following reaction scheme



The value of the activation entropy provides evidence against the formation of a solvated ion pair as intermediate or transition state. The mechanism of the reaction pathway a is discussed.

References

1 H. H. Limbach and W. Seiffert, *J. Am. Chem. Soc.*, in press.
2 H. H. Limbach, *J. Magnetic Reson.*, *36* (1979), in press.
3 D. Gerritzen and H. H. Limbach, *J. Phys. Chem.*, in press.

Solvent Effects on Some Optical and Spectroscopic Properties of Aromatic Compounds

J. F. KERUZORE

Laboratoire de Chimie de Coordination, F31030 Toulouse Cedex, France

C. CLEMENT

Centre de Recherche Paul-Pascal, F33405 Talence, France

and J. P. CANSELIER

Institut du Génie Chimique, F31078 Toulouse Cedex, France

In this work we want to report some solvent effects observed during studies on benzenoid and heterocyclic compounds by the Faraday effect and Depolarized Rayleigh Scattering (DRS), and their TCNE-complexes, by UV–visible spectrophotometry.

The measured properties, respectively molecular magnetooptical rotation ($[\rho]_M$), molecular optical anisotropy (γ^2) and maximum absorption wavenumber ($\bar{\nu}_{max}$) undergo rather large changes when moving from gas phase to pure liquid or dissolved state, and vary weakly from a solvent to another one.

As regards weak interactions, the Faraday effect allows essentially to observe internal field changes (Lorentz correction). It is likely that this bulk effect is not restricted to 'aromatic' solutes. Moreover most solute–solvent interactions are masked by this non-specific medium effect, since even with polar solvents ($CHCl_3$, alcohols) no specific interaction given by π-donors and/or polar solutes (*e.g.* halobenzenes, anisole, ...) is detected. So, for a given substance, the true value of $[\rho]_M$ is obtained in the pure liquid state or in a solvent as refractive as the solute.

On the contrary, DRS, very sensitive to oriented interactions, can detect diatropism or paratropism in liquids. Therefore, to get comparable, 'intrinsic' γ^2 values one must not work with pure liquids but rather with dilute solutions in the same 'inert' solvent, that is a non-polar, weakly anisotropic one, containing bonds of the same kind as the solute. Accordingly, for organic compounds (C–H bonds), cyclohexane is preferred to CCl_4 (which may also give specific interactions). On the other hand the molar volume of the solvent need not be taken into account. The cases of benzene and some heterocyclics illustrate these principles.

Finally, spectrophotometric studies of molecular complexes show that the influence of non-polar solvents on $\bar{\nu}_{max}$ generally reduces to a gross medium effect involving a linear function of $(n^2 - 1)/(2n^2 + 1)$. As regards polar solvents, more complex interactions with aromatic compounds and acceptor are likely to occur, and no correlation can be found with polarity parameters like Z or E_T. TCNE-complexes of benzene, benzothiophene (after deconvolution of spectra) and dibenzothiophene are considered.

Two Photon Absorption and Excited Fluorescence of 2,2′-Bipyridine

E. CASTELLUCCI and P. R. SALVI

Istituto di Chimica Fisica dell'Università, Via G. Capooni 9, 50121-Florence, Italy

Two-photon absorption spectroscopy is proving a powerful method to probe one-photon forbidden