

On the $n-\pi^*$ Blue Shift Accompanying SolvationMati Karelson[†] and Michael C. Zerner^{*}Quantum Theory Project, Department of Chemistry
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It is well-known that compounds containing lone pairs undergo a blue shift (higher energy) in their $n-\pi^*$ electronic transition upon solvation. The reason generally put forth to explain such a blue shift is that the lone pair, because of its spacial extent, interacts with the solvent, either weakly, as in aprotic solvents, or strongly through the direct formation of hydrogen bonds, as with water or alcohols.¹⁻³ This interaction is either inductive, through the donation of electrons to a solvent molecule, or bonding. In either case the lone-pair orbital is lowered in energy. The π^* orbital is less affected, although arguments can be made suggesting that this orbital is slightly lowered in energy and helps contribute to the slight red shift often observed in the $\pi-\pi^*$ spectrum.

It is the purpose of this communication to suggest that this explanation is at best incomplete and, in many cases, incorrect. We offer here an alternate explanation, equally as simple and equally as appealing. We consider a molecule with a dipole moment dissolving in a medium of dielectric constant ϵ and index of refraction n_D . According to reaction field theory⁴⁻⁷ the solute induces a dipole in the solvent proportional to its own dipole μ , $\Gamma(\epsilon, n_D)\mu$, where $\Gamma(\epsilon, n_D)$ is the proportionality factor dependent on the dielectric permittivity ϵ and refraction index n_D of the solvent.⁸ In this theory as we implement it, the Fock operator is corrected by⁸⁻¹⁰

$$\hat{f} = \hat{f}_0 - 2\Gamma(\epsilon, n_D)\bar{\mu}_0\mu$$

with $\bar{\mu}_0$ the ground-state dipole as calculated self-consistently. The total energy of the ground state as calculated from the quantum mechanics with this Fock operator is then corrected for the energy lost by the solvent in dissolving the solute:

$$\Delta E_0 = \langle \psi_0 | H | \psi_0 \rangle + \Gamma(\epsilon, n_D)\bar{\mu}_0\mu$$

The interaction energy of the excited state is similarly expressed, but because absorption is a process quicker than solvent reorientation, the stability of the excited state is given as follows:

$$\Delta E^* = \langle \psi^* | H | \psi^* \rangle + \Gamma(\epsilon, n_D)\bar{\mu}^*\bar{\mu}_0 - \Upsilon(n_D)(\bar{\mu}_0 - \bar{\mu}^*)\bar{\mu}^*$$

The first term is the correction assuming no solvent relaxation upon excitation, whereas the second term, usually much smaller than the first, accounts for the electronic polarization of the medium, which does follow the excitation process.

Most molecules that possess lone-pair orbitals have sizable dipole moments, with the negative end of the dipole pointed in

Table I. INDO/S SCRF-CI Calculated and Experimental¹³ Spectral Transition Energies of Some Heterocycles in Different Media^a

molecule	solvent	ϵ	n_D	$\nu_{\text{calcd.}} \text{ cm}^{-1}$	$\nu_{\text{expt.}} \text{ cm}^{-1}$
pyrimidine	gas phase	1.000	1.0000	32 966	—
	isooctane	1.940	1.3915	33 559	34 200
	diethyl ether	4.355	1.3527	34 127	34 400
	acetonitrile	37.50	1.3416	34 697	34 800
	water	80.10	1.3330	34 743	36 900
	2H ₂ O	1.000	1.0000	30 982	36 900
pyridazine	water + 2H ₂ O ^b	80.10	1.3330	36 572	36 900
	gas phase	1.000	1.0000	28 329	—
	isooctane	1.940	1.3915	29 460	29 740
	diethyl ether	4.355	1.3527	30 382	30 150
	acetonitrile	37.50	1.3416	31 296	31 080
	water	80.10	1.3330	31 368	33 570
pyrazine	2H ₂ O	1.000	1.0000	26 490	33 570
	water + 2H ₂ O	80.10	1.3330	33 927	33 570
	gas phase	1.000	1.0000	30 387	—
	isooctane	1.940	1.3915	30 387	31 610
	diethyl ether	4.355	1.3527	30 387	31 610
	acetonitrile	37.50	1.3416	30 387	31 740
	water	80.10	1.3330	30 387	33 160
	2H ₂ O ^c	1.000	1.0000	32 900	33 160
	water + 2H ₂ O ^d	80.10	1.3330	33 301	33 160

^aThe cavity radii for the heterocycle molecules in solution were estimated from their mass densities as 2.6 Å. The radii for the hydrogen-bonded complexes of heterocycles with two water molecules were calculated as 2.75 Å. ^bThe calculation gives two close transitions at 35 465 and 37 678 cm⁻¹ of equal oscillator strength. The mean value of transition energy is given in the table. ^cThe calculation gives two close transitions at 30 505 and 33 562 cm⁻¹ of unequal oscillator strength. The weighted mean value of transition energy is given in the table. ^dThe calculation gives two close transitions at 30 120 and 33 929 cm⁻¹ of unequal oscillator strength. The weighted mean value of transition energy is given in the table.

the direction of the lone pair. Excitation from this orbital to the delocalized π^* orbital generally reduces the dipole moment of the molecule considerably. The interaction with the dielectric medium lowers the ground-state energy of the solute molecule then substantially more than it lowers the excited-state energy, and this is the origin of the blue shift. We have quantified this idea, including the reaction field into the quantum-mechanical Hamiltonian in a self-consistent field fashion.¹¹ In Table I we present our calculated shifts for pyrimidine using the INDO spectroscopic model (INDO/S, an SCF-CI theory¹²). The self-consistent reaction field, that is, the polarization of the medium alone, explains all the shifts, except that observed in water. Water and acetonitrile are predicted to produce about the same blue shift. Explicitly H bonding two water molecules to the N lone pairs of pyrimidine without surrounding polarizable medium leads to a calculated red shift! Treating the entire complex, pyrimidine and two bound water molecules, in the reaction field leads to a predicted shift of 3000 cm⁻¹, in good agreement with experiment (cf. Table I).

Analogous results were obtained for the pyridazine and pyrazine molecules. The latter molecule has a zero dipole moment in both ground and excited states, and thus only small solvatochromic shifts are observed experimentally in non-hydrogen-bonded solvents (cf. Table I). However, our calculation of the complex of pyrazine with two water molecules in the presence of the reaction field of bulk water characterized by macroscopic dielectric permittivity is in excellent agreement with the experimentally observed blue shift whereas the treatment of an isolated complex gives the shift in the wrong direction. Therefore the origin of the solvatochromic blue shift of $n-\pi^*$ transitions in organic molecules in aprotic solvents can be explained by the simple dielectric effect model. The shifts that occur in hydrogen-bonding

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solvents are complex and depend both on the solute-solvent hydrogen bonding and dielectric relaxation. The heteroatom lone pair hydrogen bonding in the absence of dielectric effects can often lead to red shifts.

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α "Agostic" Assistance in Ziegler-Natta Polymerization of Olefins. Deuterium Isotopic Perturbation of Stereochemistry Indicating Coordination of an α C-H Bond in Chain Propagation

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The well-defined, homogeneous Ziegler-Natta olefin polymerization systems that have been reported recently provide an unprecedented opportunity to investigate the mechanism of this important process. New systems¹ include (1) single-component catalysts such as cationic group 4 metallocenes² or the isoelectronic, neutral group 3 or lanthanide metallocene hydrides or alkyls³ and (2) highly active, two-component systems consisting of "methylalumoxane" in combination with a group 4 metallocene derivative, which, with suitable modification of the cyclopentadienyl ligands, may exhibit remarkable iso- or syndiospecificities.⁴ While a consensus appears to be developing that in all these systems the active catalysts are the 14-electron, d^0 (or d^0f^n) metallocene alkyls, Cp_2MR (M = lanthanide or group 3 transition metal) or $[Cp_2MR]^+$ (M = group 4 transition metal), the mechanism for chain propagation and the geometry of the transition state for olefin insertion into the metal-carbon bond have not yet been unequivocally established.

The Cossee mechanism and a staggered arrangement of alkyl and olefin substituents (A) generally have been assumed in rationalizing the stereospecificity of propene polymerization by these metallocene catalyst systems.⁵ The most popular alternative suited to d^0 metal complexes, the "modified Green-Rooney mechanism",

(1) A class of one-component ethylene-polymerization catalysts based on late-transition-metal complexes of the type $(\eta^5-C_5Me_5)(L)M(C_2H_5)(R)]^+$ (M = Co, Rh; L = phosphine or phosphite) has also been developed. See: Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634-5636 and references cited therein.

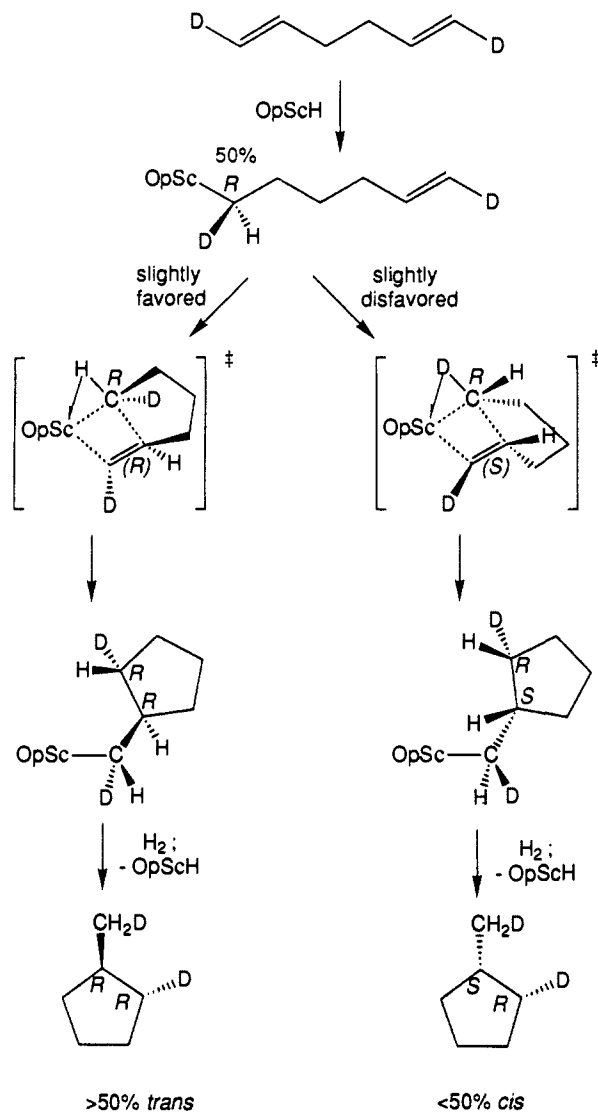
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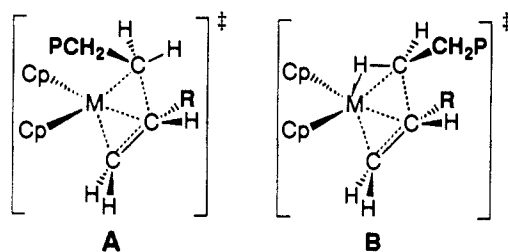
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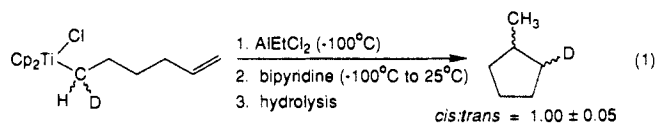
Scheme I



invokes α C-H coordination to assist olefin insertion,⁶ a quite different transition-state geometry (B).



In a cleverly conceived experiment, Grubbs et al.⁷ probed for an α agostic interaction in the transition state for olefin insertion. Racemic 1-d₁-5-hexenylchlorotitanocene was prepared and found to undergo $AlEtCl_2(CH_2CH_3)$ -induced cyclization to a mixture of *cis*- and *trans*-2-d₁-cyclopentylmethyl stereoisomers (eq 1). Any



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