the system is not fully understood. Rather it denotes the distribution of the hydrogen atoms which ensues because of the rapid equilibration of **7**, **10**, and 11.

(18) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinhelm/Bergstr., Germany, 1970, p 114.

(19) The isomerization can equally be formulated as a two-step process, occurring via successive 1,2- and 1,4-hydride shifts (see ref 1); it is most simply formulated as a 1,3-hydride shift, although which route requires the lower activation energy is not known.

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Excited-State Solvation vs. Ground-State Solvation in the n → π* Solvent Blue Shift of Ketones and Azo Compounds[1]

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Abstract: The enthalpies of transfer from one solvent to another of the n → π* Franck-Condon excited states of some ketones and azo compounds were determined by combining calorimetric and spectroscopic data. It was found that the enthalpy of transfer of the ground state and of the excited state into the blue shifted solvent could be either exothermic or endothermic. Examples of all three possible combinations were found and are described. The total solvation energy of the acetone n → π* excited state in six solvents is reported.

The blue shift of n → π* transitions on going to more polar solvents is one of the oldest and most reliable rules in the electronic spectroscopy or organic compounds.[2] It has been utilized to distinguish n → π* transitions.[3] One explanation of this phenomenon has been that the blue shift is caused by stabilization of the polar ground state in the more polar solvent. In those cases where the more polar solvent is a hydrogen bond donor, the formation of a hydrogen bond with the n-electrons is then considered to lower the energy of the n-orbital by an amount equal to the blue shift relative to a nonhydrogen bonding solvent.[4] On the other hand, part of the blue shift could arise from the destabilization of the Franck-Condon excited state in the hydrogen bonding solvent.[6]

These two possible effects can be distinguished and their relative importance evaluated by comparing the enthalpy of transfer from one solvent to another of the ground state, $\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$ with the energy of transfer of the Franck-Condon excited state, $\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, and seeing the extent to which the solvent blue shift, $\delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, is influenced by changes in the solvation of the ground state and changes in the solvation of the excited state.

Results and Discussion

The enthalpy of solvent transfer of a compound, $\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, is obtained by measuring its heat of solution, ΔH_{S} in the two solvents of interest

$$\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}} = \Delta H_{\text{S2}} - \Delta H_{\text{S1}}$$

With the solvent blue shift $\delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}}$, defined in the usual way as the difference in the excitation energies, $\Delta E^{\text{n}\rightarrow\pi^*}$, in the two solvents

$$\delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}} = \Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 2}} - \Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}}$$

the energy of transfer of the Franch-Condon excited state, $\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$ is then readily calculated by eq 1.

$$\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}} = \delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}} + \delta\Delta E^{\text{n}\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}} \qquad (1)$$

Ketones. The blue shift of acetone and benzophenone on going from a nonpolar to a hydrogen bonding solvent (Table I and Figure 1) is evidently a cooperative effect. Comparable contributions to the blue shift are made by an *exothermic enthalpy of transfer into the protic solvent of the ground state and an endothermic enthalpy of transfer into the protic solvent of the excited state.* The former effect, attributable to the lowering of the n-orbital energy by hydrogen bonding, accounts for only half or less of the observed effect. The rest is attributable to Franck-Condon orientation strain,[5a] i.e., the fact that the carbonyl group dipole finds itself in a solvation shell which was optimal for the ground state, but is not optimal for the substantially diminished excited state carbonyl dipole.

The blue shifts of ketones on going from a dipolar aprotic to a polar protic solvent (Table I and Figure 2) present a very different picture. Enthalpies of transfer of both *ground states and excited states are endothermic into the protic ("blue") solvent.* The net interaction[6] between the carbonyl dipole and the solvent being less in the protic than in the dipolar aprotic solvent, the ground state contribution alone would predict a red shift of the n → π* transition on going to the protic solvent. The observed blue shift is caused by the fact that the orientation strain in the Franck-Condon excited state is evidently greater in the hydrogen bonding solvents than it is in the dipolar aprotic solvents. A possible way of accounting for this might be found in the difference in the nature of the solvent-solute dipole-dipole interactions present in the two kinds of solvents. The most plausible dipole-dipole alignment existing between a carbonyl solute and a dipolar aprotic solvent (a carbonyl or cyano compound) would include the side-by-side head-to-tail arrangement shown in Figure 3, left. On the other hand, the lowest energy interaction between a carbonyl group and a hydrogen bond donor is the linear head-to-tail arrangement (Figure 3, right).[7] Decrease of the solute dipole moment on going to the n → π* excited state would lead to a greater loss of electrostatic and polarization interaction energy in the linear case than in the side-by-side case. This would lead to a greater Franck-Condon orientation strain in the protic solvent than

Table I. The Solvent Blue Shift ($\delta\Delta E^{n\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}}$) of Ketones and the Energy of Solvent Transfer of Their Ground States ($\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$) and Their n → π* Excited States ($\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$) (in kcal/mol)

Compound	Solvent transfer	$\delta\Delta E^{n\rightarrow\pi^*}_{\text{solvent 1}\rightarrow\text{solvent 2}}$	$\delta\Delta H^{\text{ground state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$	$\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$
Acetone	Carbon tetrachloride → water	5.86[a,b]	−3.16[c,d]	2.70
Benzophenone	Hexane → ethanol	3.46[a]	−0.97	2.49
Benzophenone	Methyl acetate → ethanol	2.26[a]	0.97	3.23
Benzophenone	Acetonitrile → ethanol	1.46[a]	0.25	1.71
Acetophenone	Dimethylformamide → methanol	2.02	1.34[e]	3.36
2-Acetonaphthone	Dimethylformamide → methanol	0.43	1.60[e]	2.03

[a] M. Ito, K. Inuzuka, and S. Imanishi, *J. Am. Chem. Soc.*, **82,** 1317 (1960). [b] P. Maroni, *Ann. Chim. (Paris)*, **13,** 757 (1957); J. E. Dubois, E. Goetz, and A. Bienvenue, *Spectrochim. Acta*, **20,** 1815 (1964). [c] J. W. Larsen, *J. Am. Chem. Soc.*, **92,** 5136 (1970). [d] E. M. Arnett, *J. Am. Chem. Soc.*, **88,** 2598 (1966). [e] Data from ref 7.

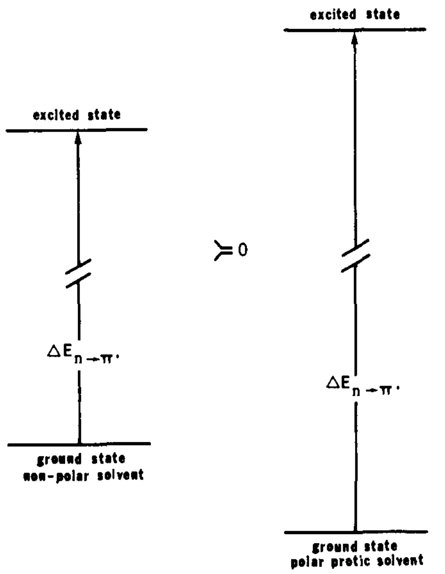

Figure 1. Relative energies of the ground states and the n → π* excited states of ketones in a nonpolar solvent and in a hydrogen bonding solvent.

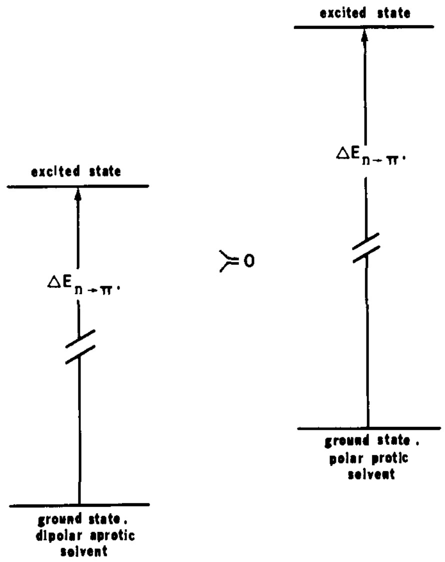

Figure 2. Relative energies of the ground states and the n → π* excited states of ketones in a dipolar aprotic solvent and in a polar protic solvent.

in the dipolar aprotic solvent and hence to an increase in the (endothermic) transfer enthalpy of the excited state into the protic solvent ($\delta\Delta H^{\text{excited state}}_{\text{solvent 1}\rightarrow\text{solvent 2}}$.

The above discussion treats the interaction between the carbonyl dipole and the solvents as the principal interaction determining the solvent transfer enthalpies of the ground states and the excited states. An objection might be raised, namely that the magnitudes of the transfer enthalpies are determined mainly by parts of the solute molecule other than the functional group in which the electronic restructuring mainly takes place when light is absorbed. Then, treating only the interaction between that functional group and solvent would be a poor approximation. Large interactions between the carbonyl group and the more protic solvent might then be masked by equally large interactions of other parts of the molecule with the dipolar protic solvent. However, this is definitely not the case. Consider, for example, acetophenone $\delta\Delta H^{\text{ground state}}_{\text{DMF}\rightarrow\text{CH}_3\text{OH}} = 1.34$, $\delta\Delta H^{\text{excited state}}_{\text{DMF}\rightarrow\text{CH}_3\text{OH}} = 3.36$. The enthalpy of transfer of the "other parts" of the molecule could be approximated by ethylbenzene. However, ethylbenzene has a negligibly small value of solvent transfer, $\delta\Delta H^{\text{ground state}}_{\text{DMF}\rightarrow\text{CH}_3\text{OH}} = -0.15$. Clearly the magnitude and the direction of solvent transfer enthalpies of ground and excited states of these ketones is determined by interactions between the functional groups and the two solvents. Examination of the group transfer enthalpies of Fuchs and Rodewald[7] further supports this conclusion.

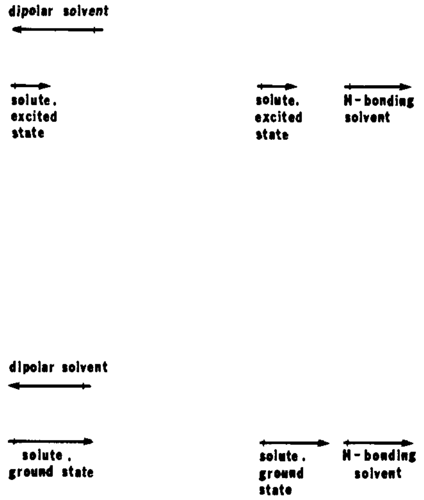

Figure 3. Solvation of carbonyl group dipoles by the dipole of a dipolar aprotic solvent (left) and by a O-H dipole (right).

Azo Compounds. The blue shift of *cis* and *trans*-azobenzene and *trans*-*p*-chlorobenzenediazocyanide on going from a nonpolar to a dipolar solvent (Table II, Figures 4, 5, and 6) shows a third type of behavior. Here both the *ground states and the excited states have exothermic enthalpies* of transfer into *the more polar ("blue") solvent*. Ground state stabilization

Table II. The Solvent Blue Shift ($\delta\Delta E^{n\to\pi^*}_{\text{cyclohexane}\to\text{cyclohexanone}}$) of Azo Compounds and the Energy of Transfer of Their Ground States ($\delta\Delta H^{\text{ground state}}_{\text{cyclohexane}\to\text{cyclohexanone}}$) and Their n → π* Excited States ($\delta\Delta H^{\text{excited state}}_{\text{cyclohexane}\to\text{cyclohexanone}}$) from Cyclohexane to Cyclohexanone (in kcal/mol)

Compound	$\delta\Delta E^{n\to\pi^*}_{\text{cyclohexane}\to\text{cyclohexanone}}$	$\delta\Delta H^{\text{ground state}\ a}_{\text{cyclohexane}\to\text{cyclohexanone}}$	$\delta\Delta H^{\text{excited state}}_{\text{cyclohexane}\to\text{cyclohexanone}}$
cis-Azobenzene	0.52	−2.97	−2.45
trans-Azobenzene	0.21	−1.96	−1.75
trans-*p*-Chlorobenzenediazocyanide	1.53	−2.94	−1.41

[a] Data from P. Haberfield, P. M. Block, and M. S. Lux, *J. Am. Chem. Soc.*, **97**, 5804 (1975).

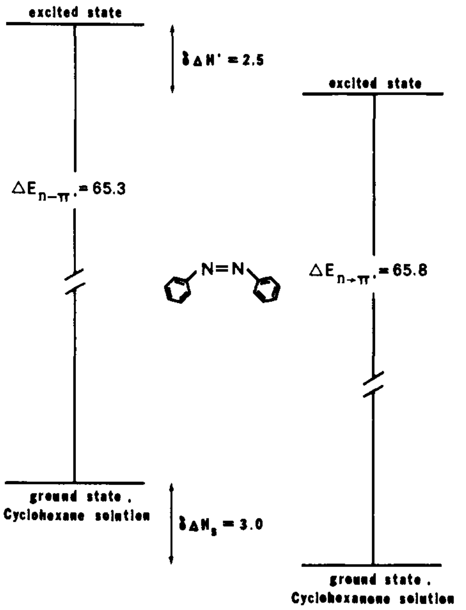

Figure 4. Relative energies (kcal/mol) of the ground states and the excited states of *cis*-azobenzene in cyclohexane and cyclohexanone solvent.

Table III. The Solvation Blue Shift ($\delta\Delta E^{n\to\pi^*}_{\text{vapor}\to\text{solvent}}$) of Acetone, the Enthalpy of Solvation of the Acetone Ground State ($\Delta H^{\text{ground state}}_{\text{solv}}$) and the Enthalpy of Solvation of the Acetone n → π* Excited State ($\Delta H^{\text{excited state}}_{\text{solv}}$) (in kcal/mol)

Solvent	$\delta\Delta E^{n\to\pi^*}_{\text{vapor}\to\text{solvent}}$ [a]	$\Delta H^{\text{ground state}}_{\text{solv}}$ [b]	$\Delta H^{\text{excited state}}_{\text{solv}}$ [c]
Benzene	0.00	−7.06	−7.06
Carbon tetrachloride	0.00	−6.58[d]	−6.58
Chloroform	1.11	−9.28	−8.17
Acetone	1.86	−7.37	−5.51
Methanol	4.18	−6.87	−2.69
Water	5.78	−9.74[e]	−3.96

[a] Data from H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967, p 99. [b] $\Delta H^{\text{ground state}}_{\text{solv}} = \Delta H_s - \Delta H_{\text{vap}}$ where ΔH_s is the heat of solution of acetone in the solvent, ΔH_s = 0.31 (benzene), −1.91 (chloroform), 0.50 (methanol), and ΔH_{vap} is the heat of vaporization of acetone, ΔH_{vap} = 7.37 (at 25.0 °C); data from "International Critical Tables", Vol. 5, McGraw-Hill, New York, N.Y., 1928, pp 138, 148, and J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y. (1970). [c] $\Delta H^{\text{excited state}}_{\text{solv}} = \Delta H^{\text{ground state}}_{\text{solv}} + \delta\Delta E^{n\to\pi^*}_{\text{vapor}\to\text{solvent}}$. [d] ΔH_s = 0.79, J. W. Larsen, *J. Am. Chem. Soc.*, **92**, 5136 (1970). [e] ΔH_s = −2.37, E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966).

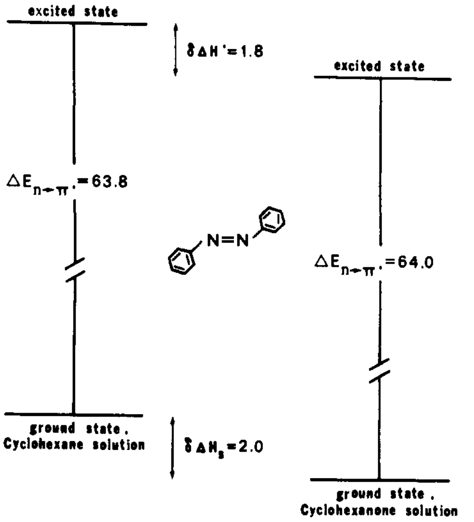

Figure 5. Relative energies (kcal/mol) of ground states and the excited states of *trans*-azobenzene in cyclohexane and cyclohexanone solvent.

Table IV. Wavelength of the Absorption Maximum for the n → π* Transition of Ketones and Azo Compounds

Compound	Solvent	$\lambda_{\max}$, nm
Acetophenone	Dimethylformamide	317.68
Acetophenone	Methanol	310.72
2-Acetonaphthone	Dimethylformamide	341.08
2-Acetonaphthone	Methanol	339.33
cis-Azobenzene	Cyclohexane	438.0
cis-Azobenzene	Cyclohexanone	434.5
trans-Azobenzene	Cyclohexane	448.03
trans-Azobenzene	Cyclohexanone	446.49
cis-*p*-Chlorobenzenediazocyanide	Cyclohexane	430.8
cis-*p*-Chlorobenzenediazocyanide	Cyclohexanone	*a*
trans-*p*-Chlorobenzenediazocyanide	Cyclohexane	435.0
trans-*p*-Chlorobenzenediazocyanide	Cyclohexanone	425.1

[a] Shoulder at about 401 nm.

by the dipolar solvent would indeed predict a blue shift (positive $\delta\Delta E^{n\to\pi^*}_{\text{cyclohexane}\to\text{cyclohexanone}}$, but of a larger magnitude than is observed.

The smaller but substantial exothermic transfer enthalpy of the excited state which exercises this damping effect on the $\delta\Delta E^{n\to\pi^*}_{\text{cyclohexane}\to\text{cyclohexanone}}$ could be caused by two factors. (1) It could involve solute-solvent interactions which are unrelated to the interaction between the n-orbitals of the azo group and the solvent. (2) It could mean that the nature of the n → π* excited state in azo compounds is such that the part of the n-orbital-solvent interaction which is retained exceeds the Franck-Condon orientation strain which is introduced.

If explanation 1 were correct then the compound having the most polar groups (in addition to the azo group) would lose the least solvent transfer energy on going to the excited state. However, this is not the case. By the same reasoning, *cis*-azobenzene, which has a net molecular dipole (μ = 3.0 D[8])

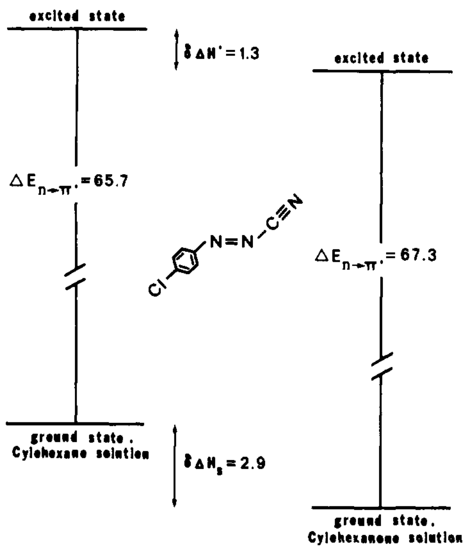

Figure 6. Relative energies (kcal/mol) of the ground states and the excited states of *trans-p*-chlorobenzenediazocyanide in cyclohexane and cyclohexanone solvent.

Table V. Heats of Solution (ΔH_s) of Benzophenone

Solvent	ΔH_s, kcal/mol
Hexane	6.53
Methyl acetate	4.59
Acetonitrile	5.31
Ethanol	5.56

would also be expected to lose less solvent transfer energy on going to the excited state than *trans*-azobenzene which has no net dipole moment. This also is not the case.

Therefore explanation 2 is the more likely. Even though substantial decreases in the dipole moment of the n → π* excited state of pyridazine and 9,10-diazaphenanthrene have been calculated,[9] the most likely explanation is that a substantial portion of the solvent-solute interaction in azo compounds is retained in the excited state, enough to compensate for any orientation strain that may develop.

Total Solvation Energy of the Excited State. When the absorption spectrum in the vapor phase is measurable, thus yielding the vapor to solvent shift, $\delta\Delta E^{n\to\pi^*}_{\text{vapor}\to\text{solvent}}$, eq 1 becomes

$$\Delta H_{\text{solv}}^{\text{excited state}} = \Delta H_s - \Delta H_{\text{vap}} + \delta\Delta E^{n\to\pi^*}_{\text{vapor}\to\text{solvent}}$$

where ΔH_s is the heat of the solution of the compound in a given solvent, ΔH_{vap} is the compound's heat of vaporization and $\Delta H_{\text{solv}}^{\text{excited state}}$ is the total energy of solvation[6] of the Franck-Condon excited state in that solvent. Values for the solvation energies of the ground and the n → π* excited states of acetone in several solvents are shown in Table III and Figure 7. They indicate that total solvation energies of this excited state of acetone ($\Delta H_{\text{solv}}^{\text{excited state}}$) can range down to less than half of the total solvation energy of the ground state molecule. No doubt ever greater degrees of variation are possible and it is likely that some *endothermic solvation energies* will be observed.

Experimental Section

Materials. *cis*- and *trans*-azobenzene and *cis*- and *trans-p*-chlorobenzenediazocyanide were prepared as previously described.[10] The other compounds were commercial samples which were recrystallized or distilled until their melting point or refractive index agreed with the literature value. Solvents were dried and distilled before use.

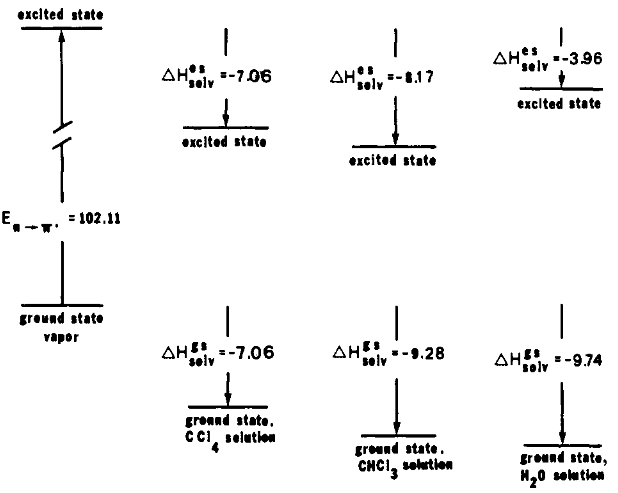

Figure 7. The total solvation energy of acetone and of the acetone n → π* excited state in three solvents in kcal/mol.

Spectroscopic Measurements. Absorption spectra were determined using a Cary 17 spectrophotometer. The wavelength of each absorption maximum was corrected by measuring the spectrum of holmium oxide glass before or after each set of runs. The values are listed in Table IV. Their accuracy is estimated to ±0.1 nm or better.

Calorimetry. Heats of solution were measured at 25.0 °C using an LKB 8700 calorimeter. Benzophenone concentrations ranged from 0.006 to 0.03 M, accuracy better than ±0.1 kcal/mol.

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(4) E.g., G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955); M. Pestemer and D. Brück in "Methoden der Organischen Chemie" (Houben-Weyl), Vol. III, Part II, E. Müller, Ed., G. Thieme Verlag, Stuttgart, 1955, p 738; S. F. Mason, *Q. Rev., Chem. Soc.*, **15**, 287 (1961); S. K. Freeman, "Interpretive Spectroscopy", Reinhold, New York, N.Y., 1965, p 31; H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967, p 99; E. F. H. Brittain, W. O. George, and C. H. J. Wells, "Introduction to Molecular Spectroscopy", Academic Press, New York, N.Y., 1970, p 46. H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Academic Press, New York, N.Y., 1961, p 187.

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(6) The net interaction energy between a solute molecule and solvent, ΔH(solute–solvent, net), is of course always the solute–solvent interaction energy, ΔH(solute–solvent), less the solvent–solvent interactions, ΔH(solvent–solvent) which must be broken in order to introduce the solute molecule into the solvent (the "hole" energy). Thus ΔH(solute–solvent, net) = ΔH(solute–solvent) − ΔH(solvent–solvent). In the discussion that follows it is always this net interaction energy which is discussed, repetitive allusions to the "hole" energy (which remains constant in the course of an electronic transition) being omitted for the sake of clarity of presentation.

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