the axial and equatorial C_1F distances as determined from the rotational constants differ by only 0.005 A, and that there is no good reason to expect that they should differ appreciably. Support for one of the more critical assumptions, that the CC bond length is the same as that of propane, is found in the electron-diffraction value[12] of the CC bond length in cyclohexane: 1.528 *vs.* 1.526 A as assumed here. Also noteworthy is that the CCC angle of cyclohexane determined by electron diffraction is 111° 33′[12] lying just between the spectroscopic values for e- and a-$C_6H_{11}F$. Finally, the stated errors are much more than adequate to account for any differences in the spectroscopic parameters and their electron-diffraction counterparts.

The relative accuracy of the results for the two isomers is quite another matter. Since the data for them has been treated in exactly the same way, errors in the differences of parameters to a large extent can be expected to cancel. Thus we believe that as the data indicate, the CCC angle is indeed slightly larger in the axial form, a result which is consistent with the notion that van der Waals repulsions between the axial fluorine atom and the axial hydrogens of carbon C_3 and C_5 may be appreciable. The indicated decrease of the HCF angle of more than 1° in going from the equatorial to the axial form is also consistent with this notion, as axial–axial repulsions might reasonably be expected to increase the corresponding interatomic distances. These same interactions should affect HCH and other angles as well, but the data are insufficient to evaluate these effects. In any event, the conclusions obtained here are relatively insensitive to assumptions about the HCH angle and CH parameters in general.[2]

It is of some interest to compare the present results with those from a microwave study of *n*-propyl fluoride by Hirota.[13] The equatorial form of $C_6H_{11}F$ is closely related to *trans*-propyl fluoride as the $FC_1C_2C_3$ and $FC_1C_6C_5$ chains are "*trans*-like." Similarly, these same chains are "*gauche*-like" in the axial form. On this basis alone it is not surprising that the dipole moment of the axial isomer was found to be 0.3 D. smaller than that of the equatorial isomer, as Hirota found the dipole moments of 2.05 and 1.90 D., respectively, for *trans* and *gauche* *n*-propyl fluoride.

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Solvent Effects on the Fluorescence Spectra of Diazines. Dipole Moments in the (n,π*) Excited States[1]

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Abstract: n ← π* fluorescence and excitation spectra as well as absorption spectra have been measured for pyridazine, pyrimidine, and pyrazine in isooctane, ether, acetonitrile, methanol, and water. The excitation spectra in the n → π* transition region resemble the corresponding absorption spectra and are shifted to the blue with increasing polarity of solvents in the same way as the absorption spectra. The dipole moments in the (n,π*) excited states are determined to be 1.1 D. for pyridazine and −0.5 D. for pyrimidine from the frequency shifts of absorption and fluorescence spectra in nonhydrogen-bonding solvents. The change of the dipole moments caused by the n → π* promotion shows that significant reorganization is engendered in the Π distribution. In hydrogen-bonding solvents, a hydrogen bond formed between solute and solvent molecules gives rise to a large blue shift in the n → π* absorption transition, but it has practically no effect upon the n ← π* fluorescence transition. It is concluded from these observations that the hydrogen bond is broken in the (n,π*) singlet excited state.

In this paper two related questions are discussed: the dipole moments of the (n,π*) singlet excited states in the diazines along with its concomitant implications to the excited-state charge distributions, and second the strength of the N···H hydrogen bond in the singlet excited states. The diazine excited-state dipole moments are of interest because of the activity in theoretical prediction of the properties of biological purines and pyrimidines. The dipole moment changes in going to the (n,π*) excited state in the diazines should serve as stringent criteria for theoretical approaches and as key quantities in energy-transfer considerations.

With regard to the first question, the simplest interpretation of the n → π* promotion is that one of the n electrons is transferred to the π* molecular orbital which is completely delocalized over the entire ring. The transition should then be accompanied by a large decrease in the dipole moment.

An estimate of the decrease can be obtained by considering the change in dipole moment (Δμ) as being approximately equal to the moment of a dipole consisting of a unit positive charge located at the centroid of the nonbonding orbital and a unit negative charge at the center of the ring (*i.e.*, assuming for simplicity that the centroid of the π* molecular orbital coincides

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[1] Supported by a grant from the National Science Foundation.

[2] (a) On leave from Hokkaido University, Sapporo, Japan. (b) School of Chemistry, Rutgers University, New Brunswick, N. J. (c) A portion of this paper represents the senior thesis of P. C. V., submitted as partial requirement for the B.S. degree, College of Science, The Pennsylvania State University, June 1965.

with the ring center). If the nonbonding orbital is represented by an sp^2 hybrid orbital, and the nitrogen 2s and 2p atomic orbitals by Slater-type orbitals with effective nuclear charge 3.90, then the centroid of the nonbonding orbital is calculated to be 0.37 A from the nitrogen nucleus.[3] Assuming that the ring is a regular hexagon with a side of 1.38 A in length, $\Delta\mu = -4.80 \cdot (1.38 + 0.37) = -8.4$ D. for pyridine, $\Delta\mu = -8.4 \cdot (\cos 30°) = -7.3$ D., and $\Delta\mu = -8.4(\cos 60°) = -4.2$ D. for pyridazine and pyrimidine, respectively.

The magnitudes of the estimated moment changes are so large that not only should they be easily observable but also any significant reorganization of the Σ and Π distributions including rehybridization of the nonbonding orbitals should be detectable.

With regard to the second question, that hydrogen bonding plays a role in the blue shift of $n \rightarrow \pi^*$ transitions was established by Brealey and Kasha.[4] Pimentel[5] made clear the importance of the Franck–Condon principle, applied to the potential curves of the hydrogen bond. Krishna and Goodman[6] then established that the hydrogen bond either does not exist or is very weak for the (n,π^*) triplet states of pyrazine and pyrimidine. The total picture is that the $n \rightarrow \pi^*$ absorption transition undergoes a blue shift corresponding to the energy of the hydrogen bond formation in the ground state plus the destabilization energy due to the Franck–Condon effect. To complete the picture it is necessary to ascertain the factors that cause the weakness of the hydrogen bond in the excited state. It is widely accepted that this is caused by the spatial removal of one of the lone-pair electrons, but to give a definitive account it is necessary to show that the hydrogen bond is broken for *singlet* (n,π^*) states.

In molecular emission spectroscopy it has been accepted as a general rule that fluorescence is quenched for molecules in which the lowest singlet excited state is of an (n,π^*) type.[7,8] Recently, however, Börresen[9] found an emission in fluid solutions of pyrimidine and attributed this to fluorescence. Cohen, Baba, and Goodman[10] observed a weak emission from pyridazine as well as pyrimidine in hydrocarbon solutions. On the basis of experimental results for excitation spectra, mirror-image relationship, lifetimes, polarization, and substituent effects, they reached the conclusion that the emissions originate in pyridazine and pyrimidine themselves and are from the lowest (n,π^*) singlet state. Furthermore, Logan and Ross[11] showed that pyrazine is fluorescent both in solid solution and as a vapor.

As is well known, the effect of polar solvents on the energy of the absorption and fluorescence transitions can be used for evaluating the dipole moment in the excited state associated with the transition.[12] An example of this procedure is found in the investigation of Ito, *et al.*,[13] of the dipole moment in the (n,π^*) singlet state for several carbonyl compounds. In the carbonyl case no fluorescence was observable, and the lack of any fluorescence data made it difficult to determine the dipole moment value unambiguously. However, for the diazines we are now in a position to utilize the solvent shifts of the fluorescence bands to obtain the dipole moments of the (n,π^*) states.

Experimental Section

A. Materials. Pyridazine (Aldrich Chemical Co.), pyrimidine (Nutritional Biochemicals Corp.), and pyrazine (Aldrich) were purified by vacuum distillation or sublimation. Pyrimidine-d_4, obtained from Merck Sharp and Dohme of Canada, was purified by vacuum distillation.

Isooctane (2,2,4-trimethylpentane), pentane, methylcyclohexane, ether, acetonitrile, and methanol were spectroquality solvents of Matheson Coleman and Bell. All these solvents were used without further purification; it was confirmed, however, that no interfering emission was observed from these solvents.

B. Apparatus and Procedure. Absorption spectra were obtained with a Cary Model 15 spectrophotometer or a Warren Electronics Spectracord. Fluorescence measurements were made with a Baird-Atomic Model SF-1 fluorescence spectrophotometer, which consists of a 150-W xenon arc lamp, two double-grating monochromators, and a 1P28 photomultiplier tube. The emission from a 1-cm² cell was observed at 90° to the excitation beam. Wide slit widths were employed, because the fluorescences were very weak. When measuring fluorescence spectra, the band width was 32 mμ for the excitation beam and 8 mμ for the fluorescence beam, and *vice versa* in the measurement of excitation spectra. When we were concerned with resolving fine structure the 8-mμ band width was reduced to 2 mμ.

The fluorescence spectra were uncorrected, whereas the excitation spectra were corrected as follows. The spectral intensity distribution of the exciting light from the xenon lamp grating monochromator system was measured by the use of rhodamine B in ethylene glycol, making use of the independence of its fluorescence quantum yield on the wavelength of exciting light.[14] That is, the apparent excitation spectrum was measured for a dilute solution of rhodamine B, and the spectral quantum intensity distribution of the exciting light was then computed on the assumption that the true excitation spectrum follows closely the absorption spectrum expressed in terms of absorbance.[15] The result was used for the correction of the observed excitation spectra of the diazines. Because of the weakness of the fluorescence concerned, measurements of the excitation spectra had to be made in solutions of relatively high absorbance values (~0.5), so that an additional correction was necessary.[15] Taking account of the Baird-Atomic spectrophotometer construction, one may reasonably conclude that only the emitting beam emerging from a very thin layer of the solution at the center of the square cell passes through the entrance slit of the second monochromator to reach the detector effectively. A reduction of the intensity of the exciting light will occur before it arrives at this layer, due to the absorption by the solution itself. Allowance was made for this self-absorption effect of the solution on the exciting light.

Results

Absorption, fluorescence, and excitation spectra were obtained at 25° in isooctane, ether, acetonitrile, methanol, and water, the properties of the solvents being listed in Table I. Figures 1, 2, and 3 show the fluorescence, absorption, and excitation spectra for the three diazines in three solvents: isooctane, acetonitrile, and water. The absorption spectra agree with those obtained by other authors.[4,6,16,17] The arrows indicate the frequencies ν of the band maxima tabulated in Table II. For those bands exhibiting vibrational structure,

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[3] H. F. Hameka and A. M. Liquori, *Mol. Phys.*, **1**, 9 (1958).

[4] G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, 77, 4462 (1955).

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[14] W. H. Melhuish, *J. Opt. Soc. Am.*, **52**, 1256 (1962).

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[16] F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

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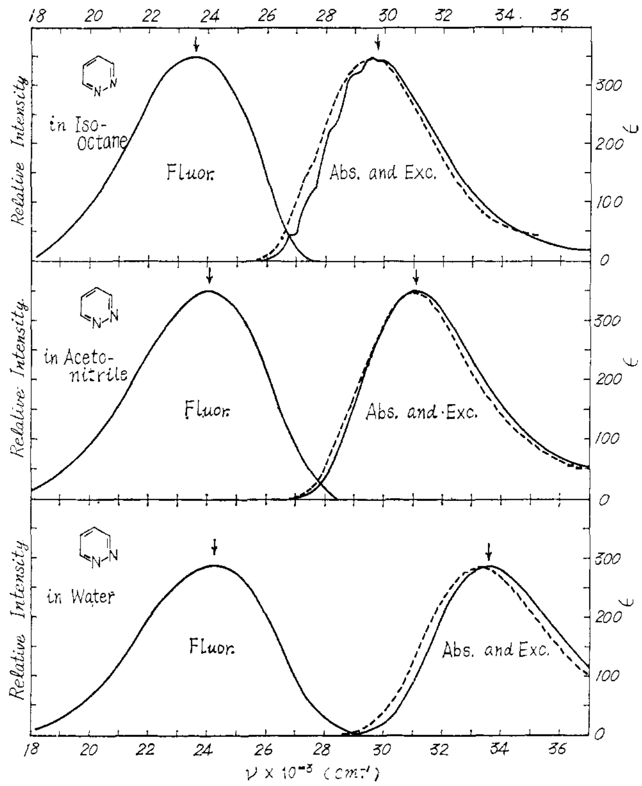

Figure 1. Fluorescence, absorption, and excitation spectra of pyridazine in isooctane, acetonitrile, and water (broken curves represent excitation spectra).

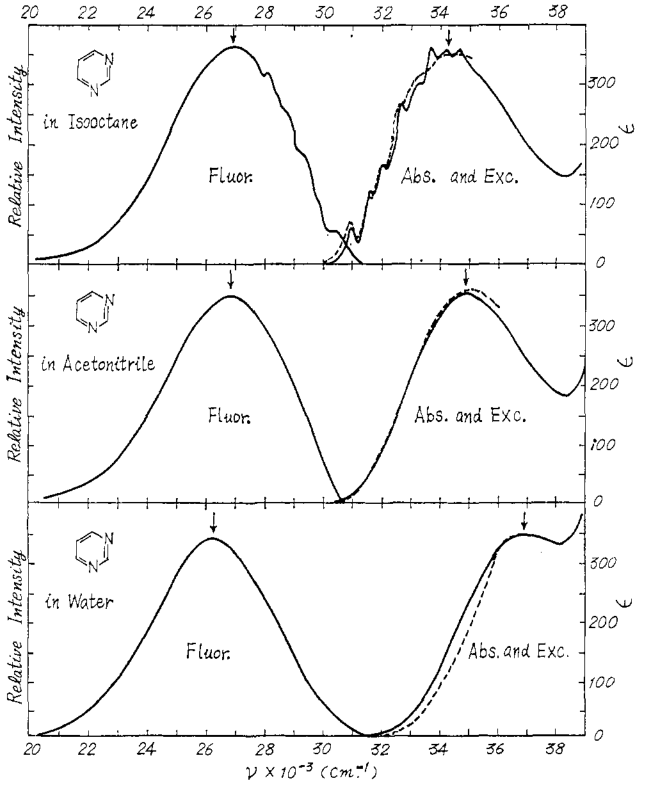

Figure 2. Fluorescence, absorption, and excitation spectra of pyrimidine in isooctane, acetonitrile, and water (broken curves represent excitation spectra).

the frequencies of the band maxima were obtained by smoothing out the structure. Such a procedure was necessary, for the 0–0 band usually could not be resolved. Table II also includes the frequency shifts, $\delta\nu$, relative to isooctane.

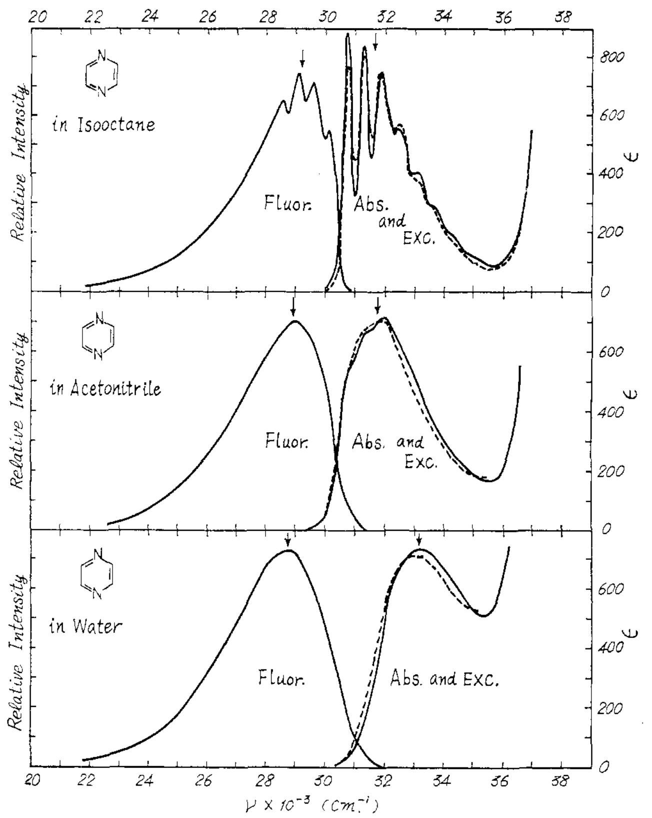

Figure 3. Fluorescence, absorption, and excitation spectra of pyrazine in isooctane, acetonitrile, and water (broken curves represent excitation spectra).

Table I. Properties of Solvents[a]

Solvent	$n^{25}\text{D}$	D^{25}	Remarks
Isooctane	1.3890	1.933	Nonpolar
Ether	1.3497	4.228	Polar
Acetonitrile	1.3416	36.7	Polar
Methanol	1.3266	32.63	Polar, proton-donating
Water	1.3325	78.54	Polar, proton-donating

[a] The values for $n\text{D}$ and D are taken from A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955; N. A. Lange, "Handbook of Chemistry," 9th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1956.

It is seen from Figures 1–3 that the excitation spectra are in agreement, within experimental error, with the corresponding absorption spectra. This is also the case with the excitation spectra in the other solvents: ether and methanol. In particular the excitation spectrum of pyrimidine and pyrazine in isooctane solution shows fine structure which is essentially the same as that found in the corresponding absorption spectrum.[18] No fine structure was found in the excitation spectrum for pyridazine in isooctane, probably because its fluorescence was so weak that the narrower slit condition could not be used.

(18) In the case of pyrimidine four vibrational peaks were observed in the excitation spectrum at lower frequencies. The intensity of the exciting light falls off rapidly with increasing frequency so that no vibrational components were observed in the region higher than 33,000 cm^{-1}.

Table II. Solvent Effects on Absorption and Fluorescence Spectra of Diazines

	Frequency, ν, and frequency shift, $\delta\nu$,[a] cm^{-1}											
	Pyridazine				Pyrimidine				Pyrazine			
	Absorption		Fluorescence		Absorption		Fluorescence		Absorption		Fluorescence	
Solvent	ν	$\delta\nu$	ν	$\delta\nu$	ν	$\delta\nu$	ν	$\delta\nu$	ν	$\delta\nu$	ν	$\delta\nu$
Isooctane	29,740	...	23,530	...	34,250	...	26,950	...	31,620	...	29,110	...
Ether	30,150	410	23,810	280	34,420	170	26,950	0	31,620	0	29,070	−40
Acetonitrile	31,080	1340	24,070	540	34,840	590	26,850	−100	31,750	130	28,940	−170
Methanol	32,360	2620	24,130	600	35,710	1460	26,810	−140	32,260	640	28,820	−290
Water	33,580	3840	24,240	710	36,900	2650	26,320	−630	33,170	1550	28,780	−330

[a] Relative to isooctane.

The spectra of pyrimidine-d_4 were also measured and were found to be similar to those of the undeuterated compound. The 0–0 absorption bands are at 30,970 and 31,090 cm^{-1}, respectively, for undeuterated pyrimidine and pyrimidine-d_4 in pentane–methylcyclohexane, 1:2 solution; that is, the 0–0 band is shifted to the blue by 120 cm^{-1} on deuteration. This blue shift was observed also in the excitation spectra in the same solvent.

It should be noted from Figures 1–3 that an approximate mirror-image relationship exists between the fluorescence and absorption spectra in all cases.

Dipole Moment in the (n,π*) Excited State

If there is no specific interaction like hydrogen bonding between solute and solvent molecules, the dispersion–dipole theory[12] of solvent effects is applicable to the frequency shifts. According to McRae,[19] the frequency shift in wavenumbers in an absorption transition is expressed as

$$\Delta\nu(\text{abs}) = (\text{dispersion term}) + \frac{1}{hc}\frac{\boldsymbol{\mu}_g^2 - \boldsymbol{\mu}_e^2}{a^3}\frac{n_D^2 - 1}{2n_D^2 + 1} + \frac{2}{hc}\frac{\boldsymbol{\mu}_g(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)}{a^3}\left[\frac{D - 1}{D + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right] \quad (1)$$

where h is the Planck constant, c is the velocity of light, $\boldsymbol{\mu}_g$ and $\boldsymbol{\mu}_e$ are the dipole moments in the ground and excited states, respectively, a is the cavity radius, and n_D and D are the refractive index for the sodium D line and dielectric constant of the solvent, respectively. In the above expression, the interaction term between the solvent permanent dipole and the solute induced dipole is neglected, and the solvent refractive index extrapolated to zero frequency is replaced by n_D. Similarly, the frequency shift in the fluorescence transition is

$$\Delta\nu(\text{fluor}) = (\text{dispersion term}) + \frac{1}{hc}\frac{\boldsymbol{\mu}_g^2 - \boldsymbol{\mu}_e^2}{a^3}\frac{n_D^2 - 1}{2n_D^2 + 1} + \frac{2}{hc}\frac{\boldsymbol{\mu}_e(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)}{a^3}\left[\frac{D - 1}{D + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right] \quad (2)$$

Define the relative frequency shift, $\delta\nu$, between two solvents, 1 and 2, as follows.

$$\delta\nu(\text{abs}) = \Delta\nu_2(\text{abs}) - \Delta\nu_1(\text{abs}) \quad (3)$$

$$\delta\nu(\text{fluor}) = \Delta\nu_2(\text{fluor}) - \Delta\nu_1(\text{fluor}) \quad (4)$$

Assuming that with these two solvents the dispersion terms and also the n values are equal, eq 1 and 2 give

$$\delta\nu(\text{abs}) = \frac{2}{hc}\frac{\boldsymbol{\mu}_g(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)}{a^3}\left[\frac{D_2 - 1}{D_2 + 2} - \frac{D_1 - 1}{D_1 + 2}\right] \quad (5)$$

$$\delta\nu(\text{fluor}) = \frac{2}{hc}\frac{\boldsymbol{\mu}_e(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)}{a^3}\left[\frac{D_2 - 1}{D_2 + 2} - \frac{D_1 - 1}{D_1 + 2}\right] \quad (6)$$

Therefore

$$\frac{\boldsymbol{\mu}_e(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)}{\boldsymbol{\mu}_g(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)} = \frac{\delta\nu(\text{fluor})}{\delta\nu(\text{abs})} \quad (7)$$

Making the reasonable assumption that the symmetry of the diazine molecules remains unchanged on electronic transition, the dipole moments $\boldsymbol{\mu}_e$ and $\boldsymbol{\mu}_g$ should be parallel to each other, although their directions may not be the same. Hence, for pyridazine and pyrimidine

$$\frac{\mu_e}{\mu_g} = \frac{\delta\nu(\text{fluor})}{\delta\nu(\text{abs})} \quad (8)$$

As pointed out by Ito, *et al.*,[13] ether and acetonitrile are a pair of solvents which seem to satisfy the conditions that the dispersion terms and n_D values should be equal (*cf.* Table I). These two solvents will be denoted by 1 and 2, respectively. Then, for pyridazine, it follows from eq 8 and Table I that μ_e/μ_g = 260 cm^{-1}/930 cm^{-1} = 0.28. By the dielectric method the ground-state dipole moment was determined to be μ_g = 3.94 D.;[20] hence μ_e = 1.10 D. and $\Delta\mu$ = −2.84 D. In a similar way for pyrimidine μ_e/μ_g = −100 cm^{-1}/420 cm^{-1} = −0.24, μ_g = 2.2 D.,[20–22] μ_e = −0.52 D., and $\Delta\mu$ = −2.72 D.

It should be noted that eq 8 does not involve any arbitrary parameters. Thus we could determine the excited-state dipole moments without assuming parameter values such as the cavity radius. On the contrary, the cavity radius a can also be determined in the following way. From eq 1 and 2

$$\Delta\nu(\text{abs}) - \Delta\nu(\text{fluor}) = \frac{2}{hc}\frac{(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)^2}{a^3}\left[\frac{D - 1}{D + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right] \quad (9)$$

Hence, for any two solvents

$$\delta\nu(\text{abs}) - \delta\nu(\text{fluor}) = \frac{2}{hc}\frac{(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)^2}{a^3}\left\{\left[\frac{D_2 - 1}{D_2 + 2} - \frac{n_{D_2}^2 - 1}{n_{D_2}^2 + 2}\right] - \left[\frac{D_1 - 1}{D_1 + 2} - \frac{n_{D_1}^2 - 1}{n_{D_1}^2 + 2}\right]\right\} \quad (10)$$

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(19) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(20) W. C. Schneider, *J. Am. Chem. Soc.*, 70, 627 (1948).

(21) W. Hückel and C. M. Salinger, *Ber. Deut. Chem. Ges.*, 77, 810 (1944).

(22) As the dipole moment value of pyrimidine, 2.42 D., was given in ref 20, and 2.0 D. in ref 21. The mean value, 2.2 D., is used in the present paper.

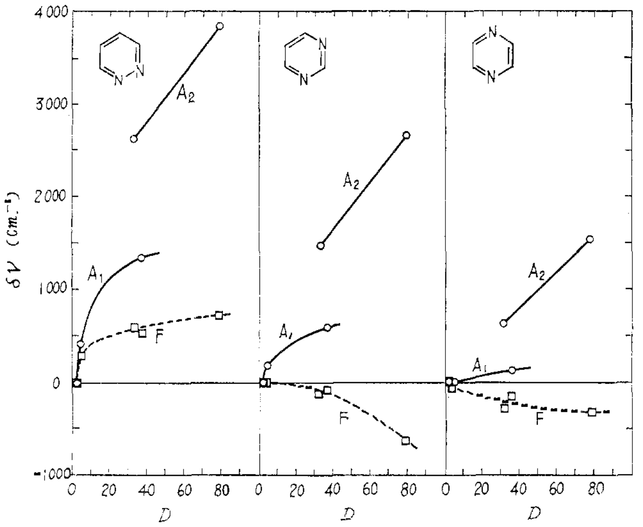

Figure 4. Plots of absorption and fluorescence frequency shifts (relative to isooctane) *vs.* dielectric constants of solvents: A$_1$, absorption in nonhydrogen-bonding solvents; A$_2$, absorption in hydrogen bonding solvents; F, fluorescence.

Since for pyridazine and pyrimidine $(\boldsymbol{\mu}_g - \boldsymbol{\mu}_e)^2 = (\Delta\mu)^2$, it follows that for pyridazine $a = 3.7$ A, and for pyrimidine $a = 3.9$ A from the data for ether and acetonitrile. These values appear to be reasonable for cavity radii of the diazines.

Discussion

A. Charge Reorganization Accompanying the h → π^* Transition. For pyrazine the molecular symmetry predicts that the dipole moment of the molecule as a whole should be zero in both the ground and the excited states. Therefore, in nonhydrogen-bonding solvents, no appreciable shifts should be produced in the n → π^* and n ← π^* transitions on increasing the polarity of the solvents. This is not quite actually the case, as seen in Table II and Figure 4. In particular a red shift is observed in the fluorescence transition relative to isooctane. The origin of this effect may be in solute (local dipole)–solvent (dipole) interaction, and because of it the determination of the dipole moment for the excited state of pyridazine and pyrimidine should be regarded as subject to error. We can say with considerable confidence that $|\Delta\mu|$ ranges between 2 and 3 D., however.

The ratio of the observed to the electrostatically calculated $\Delta\mu$ is interesting in connection with the reorganization question. The ratio is found to be $\sim$0.4 and $\sim$0.6, respectively, for pyridazine and pyrimidine. This suggests that the transferred electron is delocalized at least partially in the π^* molecular orbital, and that there is significant reorganization in going to the excited state. Rehybridization of the n orbital lowering the s character from sp^2 would decrease μ_e.[8] Assuming that the single n electron is pure p gives a rehybridization term of -1.6 and -0.9 D. for pyridazine and pyrimidine, respectively. This is substantially less than the observed decrease of >2 D., and thus no contradiction is found. The relative constancy of μ_e compared to the much greater difference in μ_g found for pyridazine and pyrimidine suggests, however, that most of the reorganization arises in the Π distribution. It is this reorganization that gives the difficulties in coming to grips with the energetics of n → π^* promotion.

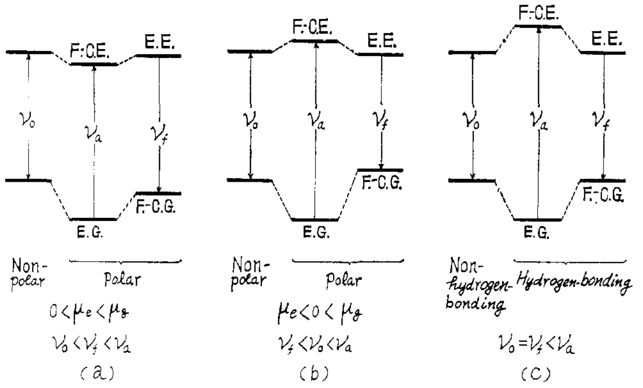

Figure 5. Energy level diagrams illustrating solvent effects on absorption and fluorescence frequencies (ν_a and ν_f). Changes of energy levels are assumed to be caused exclusively by solute dipole–solvent dipole interaction in cases a and b, and exclusively by hydrogen bonding in case c: E.G., equilibrium ground state; F.-C.G., Franck–Condon ground state; E.E., equilibrium excited state; F.-C.E., Franck–Condon excited state.

B. Frequency Shifts in Polar Solvents. The diazine n → π^* absorption bands are displaced to the blue with increasing solvent polarity, in accord with the characteristic blue shift of n → π^* transitions in polar solvents. Of the five solvents cited in Table I, methanol and water are able to form hydrogen bonds with the diazines. With these hydrogen-bonding solvents, blue shifts are observed which are anomalously larger than expected from the magnitudes of the dielectric constants of the solvents (see Figure 4).

That the situation is different in the case of n ← π^* fluorescence bands is clearly shown in Figure 4. On increasing the solvent dielectric constant they show either a red shift or a relatively small blue shift. Also, hydrogen-bonding solvents appear to have no specific effect on the fluorescence bands (*cf.* the fluorescence frequency shifts for acetonitrile and methanol).

It is worthwhile to rationalize in terms of McRae's eq 1 and 2 the frequency shifts that are produced on n → π^* and n ← π^* transitions by changing the solvent from a nonpolar to a polar substance. These are different from those on $\pi \rightarrow \pi^*$ and $\pi \leftarrow \pi^*$ transitions,[23,24] where usually $\mu_e > \mu_g$.

The changes in the energy levels of the ground and excited states due to the dipole–dipole interaction and the resulting frequency shifts are illustrated either by Figure 5a or by 5b, depending on the sign of the dipole moment of the excited state. Thus, Figure 5a applies to pyridazine in which $0 < \mu_e < \mu_g$, and Figure 5b to pyrimidine in which $\mu_e < 0 < \mu_g$. For the latter case, in the Franck–Condon excited state, the solute molecule is still surrounded by the solvent molecules whose orientation is appropriate to the ground state so that the dipole–dipole interaction leads to a raising of the energy level. Within the lifetime of the excited state, however, the equilibrium excited state will be reached in which the solvent orientation is appropriate to the excited state. The fluorescence transition will start from the equilibrium excited state for the Franck–

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[23] N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Japan*, **29**, 465 (1956).

[24] M. L. Bhaumik and R. Hardwick, *J. Chem. Phys.*, **39**, 1595 (1963).

Condon ground state. Accordingly, the absorption is expected to be shifted to the blue and the fluorescence to the red, when the solvent is changed from isooctane to ether or acetonitrile (Figure 5b). The shifts will be larger in acetonitrile than in ether, since the former has a larger dielectric constant.

It should be noted that in both pyridazine and pyrimidine the magnitude of μ_e is much smaller than that of μ_g, so that the magnitude of the fluorescence shifts is far smaller than that of the absorption shift.

C. Hydrogen-Bonding Solvents. It is reasonable to assume that the diazine molecule has no proton-accepting power in the (n,π^*) excited state because of the removal of one of the lone-pair electrons. Thus, in the equilibrium excited state the solute molecule will behave as if it were in a nonhydrogen-bonding solvent, and there should be no stabilization due to hydrogen bonding. Also, in the Franck–Condon ground state, neither stabilization nor destabilization due to hydrogen bonding should occur, since the solvent orientation cannot be favorable to the formation of a hydrogen bond between solute and solvent molecules. Therefore, apart from dipole–dipole interactions, the $n \leftarrow \pi^*$ fluorescence frequency in a hydrogen-bonding solvent is expected to be unchanged from that in a nonhydrogen-bonding solvent (Figure 5c).

The additional effect of the dipole–dipole interaction is considered to be essentially the same as discussed in the preceding subsection. In other words, solvents of this sort are best regarded as having cooperative effects of hydrogen bonding and dipolar interaction on the absorption and only the dipolar effect on the fluorescence. Figure 4 can be well understood in terms of the above. Accordingly, it may be concluded that the hydrogen bond is virtually broken in the (n,π^*) singlet state for the diazines in methanol and in water.

It is to be noted that hydrogen bonding produces a sizable blue shift in the $n \rightarrow \pi^*$ absorption of pyrazine which has no net dipole moment. This is reasonable, because hydrogen bonding is essentially local.

Solvent Effects on the Photodimerization of Coumarin[1]

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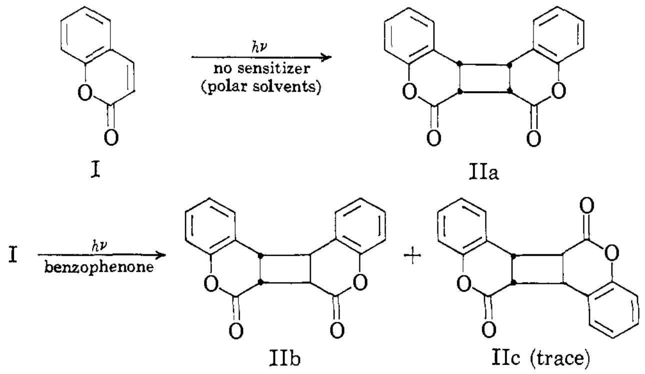
Abstract: The photodimerization of coumarin (I) has been studied in various solvents. The *anti* head-to-head dimer (IIb) is formed in nonpolar solvents to the virtual exclusion of the *syn* head-to-head dimer (IIa). The ratio of IIb to IIa decreases in polar solvents and is reversed in methanol. Conversion to IIb in a heavy-atom solvent (propyl bromide) is within experimental error of that found in *p*-dioxane and benzene. Photolysis in dilute solution favors the formation of IIb; the presence of piperylene quenches it. It is suggested that the *syn* dimer (IIa) is formed from a singlet excimer, whereas the *anti* dimer (IIb) arises *via* a monomeric triplet species.

The ability of heavy atoms (*i.e.*, atoms with high atomic numbers) to promote singlet–triplet radiationless transitions has been known for some time. While this phenomenon has been successfully utilized by spectroscopists,[2] there has as yet been no demonstration that a major change in the course of a photochemical reaction can be induced *via* this effect. The initial objective of the present work was to test for this possibility, using as our probe the photodimerization of coumarin (I).

At the time this research began,[3] it had been reported that: (a) direct irradiation of coumarin in polar solvents produced the head-to-head *syn* dimer IIa,[5] (b) irradiation of coumarin in the presence of a sensitizer (benzophenone) produced the head-to-head *anti* dimer IIb (together with trace amounts of IIc),[6] and (c) irradiation of coumarin in nonpolar solvents afforded neither dimeric product.[6,7]



These results were explained[7] by proposing that IIa is formed by the reaction of an excited singlet state of coumarin with a ground-state molecule, whereas IIb is produced by the attack of triplet coumarin on the

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[1] This work was presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] For recent discussions of the heavy-atom effect in spectroscopy, see: S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, **42**, 3060 (1965); T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965); C. E. Thompson, *J. Opt. Soc. Am.*, **55**, 1184 (1965); S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, 40, 507 (1964).

[3] Although the solvents and analytical techniques employed differ, in the main, from those used by us, Schenck and co-workers[4] have recently independently observed solvent effects analogous to those which we have reported;[1] their results will be considered together with our own in the Discussion section of this paper.

[4] C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **99**, 625 (1966).

[5] R. Anet, *Can. J. Chem.*, 40, 1249 (1962).

[6] G. O. Schenck, I. von Wilucki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1962).

[7] G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964).