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Solvent Effects on the Iodine–Pyridine Charge-Transfer Complex

Sir:

Some recent results obtained by various physical-chemical techniques indicate that the formation constant of a molecular complex is strongly solvent dependent.[1–6] However, no direct comparison has been made between values of the formation constant and physical properties of the solvents. In the present communication, we wish to present our results for the iodine–pyridine complex in various solvents, since the variation of the equilibrium constant with solvent-interaction force is significant. We shall then interpret our results on the basis of a theory developed recently by Buchowski, *et al.*[7] Finally, we shall present our analysis of solvent effects on the frequencies of free and complexed iodine absorption bands and on the energy of the charge transfer.

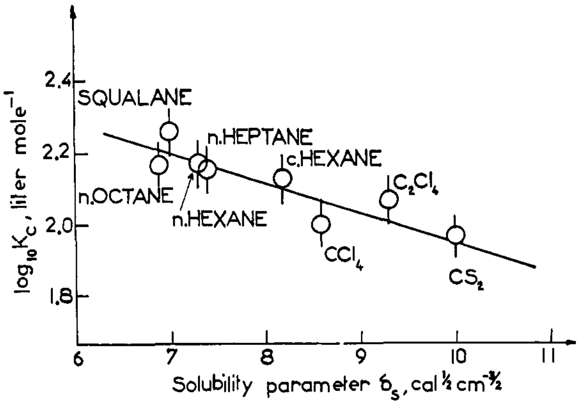

Figure 1. Plot of the logarithm of the equilibrium constant of the iodine–pyridine complex *vs.* the solubility parameter of the solvents.

Table I. Solvent Effects on the Equilibrium Constant of the Iodine–Pyridine Complex on the Iodine Bands and on the Charge-Transfer Band

Solvent	δ_s[a]	V_s, cm^3	K_c (25°), l. mole^{-1}	Log K_c	Free I_2 band, Å	Complexed I_2 band, Å	C–T band, Å
$C_{30}H_{64}$[b]	7.0		185 ± 12	2.26	5230 ± 5	4235 ± 10	2325 ± 5
i-C_8H_{18}	6.9	166	150 ± 9	2.17	5220 ± 5	4230 ± 10	2342 ± 2
n-C_6H_{14}	7.3	132	148 ± 8	2.17	5225 ± 5	4235 ± 10	2346 ± 2
n-C_7H_{16}	7.4	149	142 ± 8	2.15	5230 ± 5	4235 ± 10	2347 ± 2
c-C_6H_{12}	8.2	109	135 ± 8	2.13	5235 ± 5	4230 ± 10	2365 ± 3
CCl_4	8.6	97	102 ± 6	2.00	5175 ± 5	4170 ± 10	2425 ± 10
C_2Cl_4	9.3	103	119 ± 7	2.07	5180 ± 5	4175 ± 10	
CS_2	10.0	61	95 ± 6	1.97	5195 ± 5	4190 ± 10	
Pyridine	10.7						2450[c]

[a] Solubility parameter of the solvent, expressed in cal$^{1/2}$ cm$^{-3/2}$ (ref 13). [b] Squalane or 2,6,10,15,19,23-hexamethyltetracosane; its solubility parameter $\delta_s = 7.0 \pm 0.5$ was evaluated from its evaporation temperatures at several temperature. [c] From ref 8.

The absorption spectrum of the iodine–pyridine complex has already been examined by numerous authors.[8–10] Although the equilibrium constant of this complex in three solvents has been determined, the values were reported by three different authors and hence cannot be directly compared.

We have determined the equilibrium constant of the iodine–pyridine complex in a series of nonpolar solvents at 25° using a Cary 14 spectrophotometer. The initial concentration of iodine was 10^{-4} mole/l. while that of pyridine varied between 6.2×10^{-4} and 0.25 mole/l. The equilibrium constant K_c expressed in l./mole (Table I) was determined[11,12] by following both the decrease in intensity of the free iodine band and the increase in intensity of the complexed iodine band with increasing pyridine concentration. All the solvents chosen are nonpolar. Nevertheless, it is possible to detect significant variations of the equilibrium constant, which decreases when the interaction with the solvent increases.

According to the calculation of Buchowski, *et al.*,[7] which is based on Hildebrand–Scott theories of solutions,[13] the equilibrium constant K_c of a donor–acceptor complex can be related to the solubility parameter[13] δ_s of the solvent by the relation

$$\log K_c = a + b\delta_s$$

where a and b depend only on the properties of the donor and acceptor. In the case of the iodine–pyridine complex, the experimental results can be interpreted on the basis of this relation, as shown in Figure 1, where b is positive. When the equilibrium constant of a molecular complex increases with the solvent interaction as in the case of the trimethylamine–sulfur dioxide complex considered by Grundnes and Christian,[6] the coefficient b should have an opposite sign.

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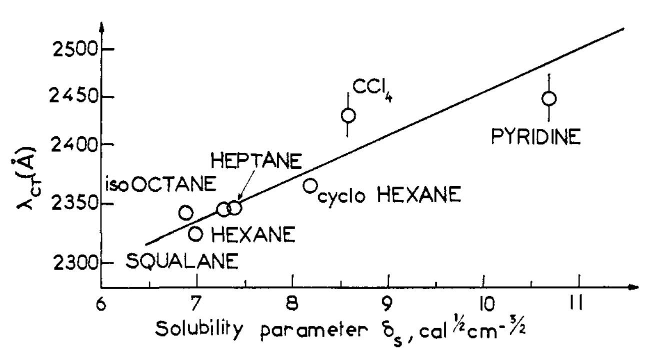

Figure 2. Displacement of the iodine-pyridine charge-transfer band with the solubility parameter of the solvents.

Furthermore, we have found that the maxima of the free and complexed iodine bands are strongly displaced in the same sense as a function of solvent (Table I). This result indicates that the iodine molecule in the complex is almost as sensitive to solvent effects as is the free molecule.

Finally, we wish to point out that the charge-transfer band of the complex is shifted significantly toward the red, corresponding to a decreasing transition energy $E_{CT} = h\nu_{CT}$, when the solubility parameter δ_s of the solvent increases (Figure 2). This result suggests that there is a larger decrease in the potential energy of the excited charge-transfer state than in that of the corresponding ground state. As δ_s is directly dependent on the vaporization energy and the molar volume of the solvent,[13] the decrease in transition energy can be correlated with both the dielectric and the cage effects of the solvent.

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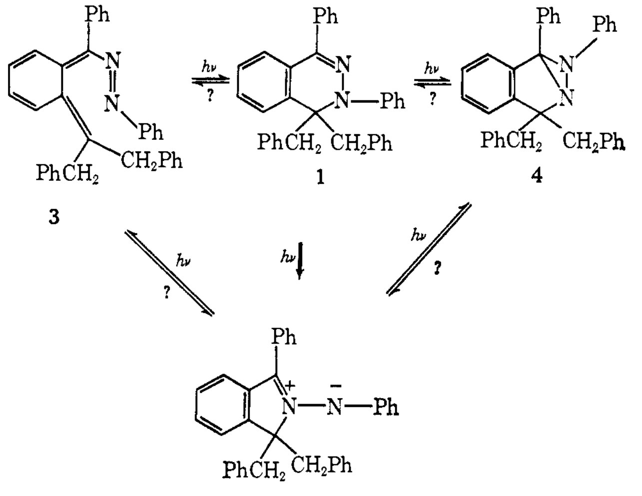
Photochemical Rearrangement of 1,1-Dibenzyl-1,2-dihydro-2,4-diphenylphthalazine. Photochemical Generation of Stable Azomethine Imines

Sir:

In an earlier communication[1] the light-induced rearrangement of a 2,3-benzoxazine was shown to produce an oxazirinodihydroisoindole. We now report what we believe is the first example of a photochemical generation of a stable azomethine imine from a 1,2-dihydrophthalazine, the nitrogen analog of the benzoxazine.[2]

Irradiation of 1,1-dibenzyl-1,2-dihydro-2,4-diphenylphthalazine [**1**;[3] $\lambda_{\max}^{\mathrm{CH_3CN}}$ 363 mμ (ϵ 8700), 246 (19,300)] in benzene solution with Pyrex-filtered light led to the formation of an orange-red compound. The reaction could be conveniently monitored by ultraviolet or nmr spectroscopy.



In the nmr spectrum[4] of the phthalazine **1**, the two benzyl groups (attached to C_1) appear as an AB quartet [**1**: nmr ($CDCl_3$) τ_A 6.77, τ_B 6.39 (q, 4 H, J_{AB} = 15.4 Hz, two CH_2Ph groups), τ 3.7–2.3 (m, 24 H, aromatic)] showing that the methylene hydrogens are magnetically nonequivalent.[5] On exposure to ultraviolet light, the original AB quartet was replaced by a second AB quartet, with slightly altered coupling constant, which grew in intensity with increased exposure time. By irradiation in benzene-diethylamine[6] (1:1, v/v) as before the azomethine imine **2** could be isolated[7] in 60–70% yield (dark red crystals with metallic luster): mp 162–163°; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 460 mμ (ϵ 10,600), 346 (9900), 265 (14,000); nmr ($CDCl_3$) τ_A 6.43, τ_B 6.13 (q, 4 H, J_{AB} = 13.0 Hz, two CH_2Ph groups), τ 2.8–2.5 (m, 24 H, aromatic).

Analytical[8] and mass spectral data for compound **2** require that it be isomeric with the starting material.[9] The ultraviolet and nmr data outlined above strongly suggest structure **2** for the photoisomer.

The azomethine imine structure **2** for the photoisomer is further substantiated by the facility with which it undergoes 1,3-dipolar additions with various dipolarophiles.[10] Treatment of **2** with dimethyl acetylenedicarboxylate in benzene solution at 60–70° yielded the

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(2) For somewhat related cases of cyclohexadiene and hexatriene photochemistry see (a) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (b) J. Meinwald and P. H. Mazzochhi, *J. Am. Chem. Soc.*, **88**, 2850 (1966); (c) W. G. Dauben and J. H. Smith, *J. Org. Chem.*, **32**, 3244 (1967); (d) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967); J. Meinwald and P. H. Mazzochhi, *ibid.*, **89**, 696 (1967); K. R. Huffman and E. F. Ullman, *ibid.*, **89**, 5629 (1967), and references therein.

(3) A. Mustafa, A. H. Harhash, and A. A. S. Saleh, *ibid.*, **82**, 2735 (1960).

(4) All nmr spectra reported here were taken on a Varian Associates 100-MHz spectrometer.

(5) This would be normally expected here because each methylene is attached to an asymmetric group. Since only one AB quartet is observed, the two CH_2's are identical, indicating coplanarity of the NPh with the remainder of the molecule. This may also be indicative of a rapid inversion of the N–Ph bond.

(6) As would be expected, the azomethine imine **2** is considerably stabilized toward further irradiation in the presence of relatively polar solvents such as ethanol, di- and triethylamines, pyridine ,and dimethylformamide. This may be due in part to the stabilization of the dipolar structure of the azomethine imine and in part due to the decreased energy of the excited state(s) of **2**. Maximum yields of **2** were obtained when irradiations were carried out in benzene–diethylamine (1:1, v/v).

(7) The red azomethine imine was extracted with a minimum volume of cold ethanol (in which **1** is virtually insoluble) followed by removal of the ethanol *in vacuo* and purification by recrystallization from ether.

(8) All new compounds reported here showed satisfactory elemental analyses and correct molecular ion peaks (M^+).

(9) The phthalazines **1** failed to show the molecular ion peak in the mass spectrum even at low voltages. The highest peak observed was at *m/e* 373, which corresponds to the loss of CH_2Ph group and not NPh group as was confirmed by high-resolution studies. Excellent elemental analyses and spectral data for **1** and its derivatives reported here confirm beyond doubt the assigned structure.

(10) For a summary of the azomethine imine reactions see R. Huisgen, *Proc. Chem. Soc.*, 357 (1961), and references cited therein.