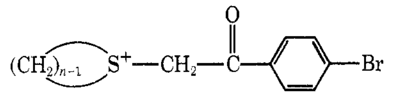
ditions partial formation of a five-membered ring apparently occurred during an attempt to obtain an intermediate six-membered ring in solvolysis of 5-chloro-1-hexyl *p*-nitrobenzenesulfonate.[5] A similar attempt to obtain a four-membered-ring iodonium ion intermediate apparently gave partial formation of the three-membered ring.[6] Furthermore, numerous attempts to obtain stable four-membered halonium ions in SbF_5–SO_2 led exclusively to three- and five-membered rings or both.[7]

Rate data (Table I, third column) emphasize the preference for three- and five-membered-ring halonium ion formation in solvolysis reactions, although participating groups not having d orbitals show a substantially similar pattern.[8] In the case of cyclic sulfonium ions, recently published rates of base-catalyzed hydrogen-deuterium exchange (Table I) provide striking odd–even effects.[9] Electron transfer from the five- and seven-membered ring carbons to sulfur can account for the increased exchange rate of the endocyclic α hydrogens. For the four- and six-membered rings electron transfer from the methyl group is facilitated, since the endocyclic orbitals are relatively ineffective in filling the d orbitals.

The last column in Table I gives data for per cent reduction of cyclic sulfoxides to cyclic sulfides by sodium hydrogen sulfite.[10] The data suggest that the rate of reduction shows alternation as ring size is incremented, althouth detailed interpretation of the multistep mechanism would be premature.

Finally, we note that pK_a data for the protonated form of sulfur containing ylides,[11] shown below, is consistent with the H–D exchange results in Table I, in that protons exocyclic to six-membered S-containing rings are more acidic than those of the comparable five-membered-ring compound.



pK_a = 7.54, n = 5 pK_a = 7.00, n = 6

The consideration mentioned above suggests a plethora of interesting experiments and theoretical investigations, covering a range of heterocycles incorporating d-orbital atoms. Several referees have pointed out that the magnitude of the interactions mentioned in this paper may be too small to dominate the chemistry of such heterocycles. However, we feel that consideration of the proposed orbital effect should be made in conjunction with studies of such heterocycles, and we accordingly present the concept in its present form. Even greater generality would obtain if the well-known general difficulty of obtaining four-membered rings[8] could be incorporated into our correlation. Possible selective stabilization of electron pairs in odd-ring orbitals having orbital dipole moments and/or large coefficients at the heteroatom deserve investigation.

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Spectroscopic Differences between Crystalline and Amorphous Phases of Indigo

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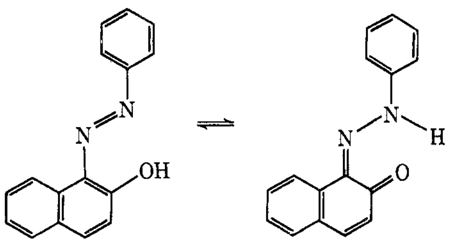
The vacuum evaporation of organic molecules has been used by a number of workers as a method of producing a desired polymorphic phase of the material.[1] It has been found for some organic systems that the amorphous state is initially formed upon vacuum evaporation and that the amorphous organic state is surprisingly stable under ambient conditions for periods ranging from days to years.[2] Of major interest are the wide variations in both spectral and electrical properties between the crystalline and amorphous phases of a given organic compound.[2] For example, the trans hydroxyazo aromatics show profound differences between the preferred species in the amorphous solid state and the crystalline phases. The lowest energy electronic transition of crystalline hydroxyazo compounds is red shifted ~1000 Å relative to that for the amorphous solid state or fluid media. This anomalous absorption characteristic of the crystalline phase has been attributed to intermolecularly hydrogen bonded hydrazone aggregates, whereas the amorphous state and solution state have been identified as being composed of a hydrazone–azo tautomeric equilibrium.[3]



Indigo has also been reported[4] to show visible absorption at considerably longer wavelengths (600–700 Å) in the solid phase than in organic solvents. From the electronic spectral observations and supporting

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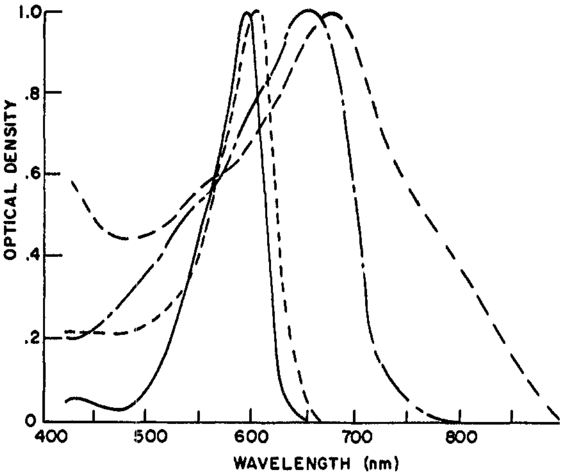

Figure 1.—Absorption spectra of indigo in ———, chloroform; --------, ethanol; ——— - ———, amorphous solid state; — — —, crystalline solid state.

infrared spectroscopic studies on model compounds, it was concluded that, in the solid state, indigo dyes are associated by means of intermolecular hydrogen bonding. While spectral shifts of dyes in solvents of different dielectric constant are well known, the spectral differences between the amorphous and crystalline phases of a given compound have received less attention. In this note are presented some comparative spectroscopic studies on indigo which clearly differentiate between the spectral properties in solution and in the amorphous and crystalline solid phases. These differences in spectral properties between the three phases can be conclusively attributed to variations in hydrogen bonding interactions. Quantum chemical calculations support the formation of associated species in the solid.

Experimental Section

Sample Preparation.—Indigo is commercially available (J. T. Baker) and was purified by recrystallization from chloroform prior to vacuum sublimation. (*Anal.* Calcd for indigo: C, 73.3; H, 3.8; N, 10.7; O, 12.2. Found: C, 73.3; H, 3.6; N, 10.9; O, 12.3.) Thin films of indigo were prepared by vacuum evaporation (10^{-5} Torr) of the purified material onto 0.5-in. diameter KBr flats and 0.5-in.-diameter quartz Suprasil windows held at ambient temperatures. The evaporations were carried out in a Bendix Balzers Model BA-3 evaporator. The thin films of indigo were determined to be amorphous by means of a polarizing microscope and X-ray diffraction techniques. Thin films of crystalline indigo were obtained by heat treating the amorphous films for 2 hr at 350°. Several crystalline samples for spectroscopic analyses were also prepared from the recrystallized material using the Nujol mull technique. Visible absorption spectra of indigo were also obtained in Matheson Coleman and Bell spectroquality chloroform and ethanol (J. T. Baker).

Spectroscopy.—The visible absorption spectra of indigo were recorded on a Cary Model 14R automatic spectrophotometer at 25°. The infrared spectra of amorphous and crystalline films of indigo were recorded on a Beckman Model IR-12 spectrometer. The visible and infrared absorption spectra of crystalline indigo were found to be identical whether the spectra were obtained in Nujol mull using the recrystallized material or from the amorphous phase crystallized directly on the optical windows.

Results and Discussion

The spectra of indigo in various media are shown for comparison in Figure 1. The wavelength maxima of

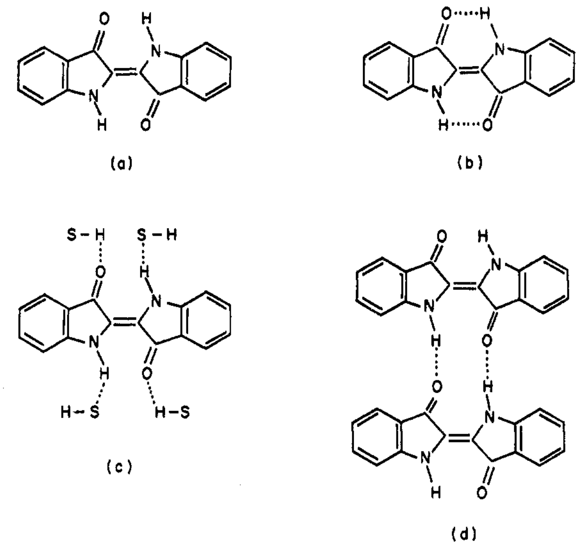

Figure 2.—Indigo with various hydrogen-bonding interactions considered.

the lowest π-π^* transition occur at 590 nm, carbon tetrachloride; 604 nm, chloroform; 610 nm, ethanol; 640 nm, amorphous solid; 668 nm, crystalline solid.[5] Weinstein and Wyman[4] have explained the strong bathochromic shift in the crystalline phase as being due to the formation of hydrogen-bonded dimers or higher polymers. In addition, X-ray crystallographic studies by von Eller[6] have also stressed the importance of hydrogen bonding in the crystalline state of indigo. In view of these findings and the wide spectral variations apparent in Figure 1, a Hückel molecular orbital (HMO) treatment of some of the factors affecting the spectrum of indigo was undertaken. The interactions involved in the calculation are illustrated in Figure 2. First, calculations were done on the free molecule (Figure 2a) using standard HMO parameters for the heteroatoms.[7] In view of the possibility of intramolecular hydrogen bonding (Figure 2b), this is then included in the calculation in the manner proposed by Pullman and Pullman.[8] The same atoms of the molecule may also be involved in intermolecular hydrogen bonding (Figure 2c) to solvent (S–H) and this is treated as was done previously for azo compounds.[9] A final possibility considered in this note is that of a hydrogen-bonded dimer (Figure 2d).

The results of the calculation are shown in Table I, where the energies (β units) of the highest occupied (HO) and lowest unoccupied (LU) orbitals are given together with their separation.

Somewhat surprisingly, the Pullman model indicates that the formation of an intramolecular hydrogen bond, case b, should increase the energy of the lowest electronic transition relative to the molecule without hydrogen bonding, case a. Thus, the strength of H

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Table I

		HO	LU	ΔE	Phase	λ_{max}, nm
(a)	No H bond	0.579	−0.021	0.600	Vapor[a]	540
(b)	Intramolecular H bond	0.640	0.000	0.640		
(c)	Intramolecular H bond	0.564	0.026	0.538	$CHCl_3$	604
					Ethanol	610
(d)	H-bonded dimer	0.612 (a_u)	0.011 (b_g^*)	0.601 ($a_u \rightarrow b_g^*$)	Crystal	560
		0.516 (b_g)	−0.013 (a_u^*)	0.529 ($b_g \rightarrow a_u^*$)		668

[a] Reference 10.

bonding decreases in the order ethanol, $CHCl_3$, and CCl_4 as reflected by the absorption maxima in these solvents. At the same time, intermolecular hydrogen bonding, case c, is indicated to decrease the energy of the lowest transition. In practice, it may not be possible to distinguish between a and b, and case a quite likely represents a hypothetical situation. It is thought that case d resembles the situation in the crystalline solid state. In the dimer, which belongs to point group C_{2h},[11] the HOMO and LUMO of the monomer are each split into dimer orbitals of a_u or b_g symmetry. The allowed[11] electronic transitions are then $a_u \rightarrow b_g^*$ and $b_g \rightarrow a_u^*$ which, as indicated in Table I, are predicted to appear at lower energies than those of the free molecule, in agreement with experimental findings. Similarly, the lower transition energy in the situation involving intermolecular hydrogen bonding is also in agreement with experiment.

The general features of the hydrogen-bonding models for the amorphous state of indigo were confirmed by infrared spectroscopy. Thus, the crystalline state is completely H bonded, as seen by the dominance of an NH bonded frequency at 3285 cm^{-1}. The infrared spectrum of the amorphous state is characterized by both free NH (3378 cm^{-1}) and bonded NH (3285 cm^{-1}) transitions. Also the carbonyl region[4] indicates that free C=O sites are in greater abundance in the amorphous state than in the crystalline phase. Therefore it is not surprising that the λ_{max} of the lowest π-π^* transition in amorphous indigo (640 nm) lies at higher energy than the crystal (668 nm). The amorphous form, most likely, represents a disordered array of the H-bonded situations shown in Figure 2.

It is pertinent to note that similar changes in spectral features do not occur where the NH moiety in indigo is replaced by O, S, or Se. In addition, indigoid molecules with bulky substituents on the 4, 5, and/or 7 positions do not show hydrogen-bonding shifts between solution and solid phases,[4] since the sterically hindering groups prevent the interaction of CO and NH groups on neighboring molecules. For example, 5,5′,7,7′-tetrabromoindigo in either $CHCl_3$ or the solid state shows no discernible difference between the peak maxima in the visible region.[4] The electronic absorption properties supported by the simple MO model do, however, clearly demonstrate that dramatic spectral differences are to be expected between the spectra of crystalline and amorphous dyes when strong H-bonding forces are the dominant intermolecular interaction.

Registry No.—Indigo, 482-89-3.

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Reactions of N-Substituted Maleamic Acids with Thionyl Chloride and Chloroacetyl Chloride

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N-Substituted maleamic acids are dehydrated to either the corresponding maleimide or the maleisoimide, depending on the dehydration conditions and the nature of the substituent.[1] When powerful dehydrating agents such as trifluoroacetic anhydride, *N,N′*-dicyclohexylcarbodiimide, or ethyl chloroformate are allowed to react with maleamic acids in the presence of triethylamine, maleisoimides are formed as the main products. Other dehydrating agents yield the corresponding imides or mixtures of imides and maleisoimides.[2] Recently N-substituted maleisoimides have been prepared using mild dehydrating agents, such as acetyl chloride, or even weak dehydrating agents, such as acetic anhydride, under controlled conditions.[1a,b] In this report the effects of thionyl chloride and chloroacetyl chloride on N-substituted maleamic acids will be presented.

The behavior of thionyl chloride toward N-substituted maleamic acids depends on the nature of the substituent and also on the temperature. A few reports have been published regarding the effects of thionyl chloride on N-substituted maleamic acids. Feuer and Rubenstein[3] reported the preparation of *N*-benzenesulfonylaminomaleimide and bismaleimide by refluxing the corresponding maleamic acids with thionyl chloride. The bismaleimide was found recently to have the bismaleisoimide structure.[4] Others[5] have utilized boiling thionyl chloride for the prepara-

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*Department of Chemistry, University of Sulaimania, Sulaimania, Iraq.

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