

Effects of High Pressures on the Absorption Spectrum of Azobenzene¹

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Abstract: The effects of high pressures (0–25 kbars) on the near-ultraviolet and visible absorption spectra of *trans*-azobenzene have been studied. Azobenzene is dispersed in six different polymer matrices and compressed in an optical cell at room temperature. The magnitude and direction of the spectral shift depend upon the type of transition ($n \rightarrow \pi^*$ vs. $\pi \rightarrow \pi^*$), the nature of the polymer matrix, and other specific interactions whose relative importance are not easily ascertained. The $n \rightarrow \pi^*$ band shows a blue shift in a hydroxylic polymer at the highest pressure. The intensity of the $\pi \rightarrow \pi^*$ band is unaffected by compression while the $n \rightarrow \pi^*$ band strength increases significantly. Such enhancement could result from partial removal of its symmetry-forbiddenness or greater intensity-stealing from the $\pi \rightarrow \pi^*$ transition at higher pressures.

The lowest electronic transitions in molecules containing chromophores such as the azo or carbonyl groups have been shown to originate from the bonding (π) or nonbonding (n) orbitals and to end in the antibonding (π^*) molecular orbital. The n orbital is localized largely on the heteroatom while the π and π^* orbitals usually characterize the entire chromophore in the absence of π conjugation in the rest of the molecule. Empirical criteria for distinguishing $n \rightarrow \pi^*$ from $\pi \rightarrow \pi^*$ transitions, relevant to the present study, have been developed for the absorption process: much lower intensities, the disappearance of fine structure, and blue shift of the band maxima in polar solvents.^{2,3} These guide lines along with others have identified the π, π^* and n, π^* character of the two transitions in the near-ultraviolet and visible spectral region for the molecule azobenzene.

Homogeneous media that have been chosen for pressure studies of $\pi \rightarrow \pi^*$ transitions in conjugated molecules are polymer matrices.^{4–9} In analogy with compressed liquid solutions,¹⁰ increasing pressures produced red shifts, relatively small changes in intensities, and considerable broadening. Only for the pseudo-aromatic molecule azulene was an initial blue shift observed for the lowest electronic transition at high pressures.^{4,11,12} The $\pi \rightarrow \pi^*$ transitions in aromatic and aza-aromatic hydrocarbons behave similarly upon compression,⁷ although differences due to the heteroatom are expected and observed. The effects of high pressures on $n \rightarrow \pi^*$ spectra of organic molecules have not been reported and are of particular interest in the present work. The $n \rightarrow \pi^*$ absorption of azobenzene in polystyrene has

been studied at atmospheric pressure.¹³ It was concluded from a Beer's law plot that a solid solution ("molecular dispersion") has been formed. It is assumed that an essentially homogeneous distribution has also been achieved in all plastics used in the present work.

The molecule *trans*-azobenzene was chosen to illustrate the effects of high pressure on the azo chromophore. This molecule, in which steric effects are absent, has two electronic transitions accessible to the high-pressure apparatus so that a comparison of pressure effects can be made for the same molecule. The strong (oscillator strength, $f \sim 0.56$)¹⁴ transition in the ultraviolet (315-m μ band) has been assigned a $\pi \rightarrow \pi^*$ transition,¹⁵ in analogy with stilbene. Both molecular orbitals are largely confined to the azo group and give rise to the color band in azo dyes.¹⁶ In the visible spectrum (~ 445 m μ) lies a weak ($f \sim 0.016$)¹⁴ broad band attributed to a transition from the n to the same π^* orbital. It has been thought that the 445-m μ band arises from two nearly degenerate n states,¹⁷ but recent polarization¹⁸ and band-analysis¹⁹ studies demonstrate that the band arises only from the higher n level which is split by $\sim 15,000$ cm⁻¹ from the lower one. Polarization data also assert that the $n \rightarrow \pi^*$ transition is symmetry-forbidden despite the relatively high intensity.³ Since it is polarized in-plane, its intensity is largely stolen from the color band.^{16,18}

The $n \rightarrow \pi^*$ transition has been studied in various liquid solvents and analyzed in terms of the magnitude and direction of shift in the band maximum. In contrast to other $n \rightarrow \pi^*$ bands, the solvent effects are small,²⁰ probably due to the absence of solute dipoles in both states. In nonpolar solvents a small red shift is observed with increasing refractive index.²¹ When the polarity and dielectric constant are increased, a blue shift is noticed

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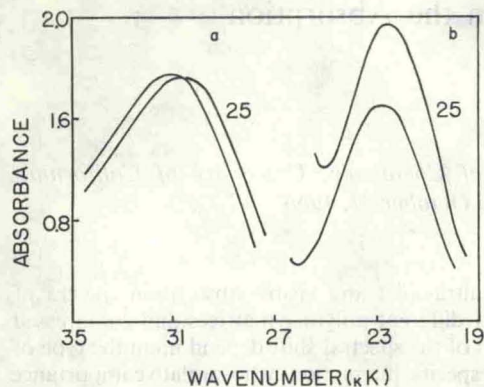


Figure 1. The absorption spectrum of azobenzene in cellulose acetate (CA) at atmospheric pressure (unlabeled curve) and 25 kbars: (a) the π - π^* band (3×10^{-3} M), (b) the n - π^* band (0.2 M).

(+400 cm^{-1} in acetonitrile relative to diethyl ether).²¹ A further blue shift in hydroxylic solvents is attributed to hydrogen bonding of ~ 1 -kcal/mole strength.²¹ Although the intensities of the bands have not been discussed as a function of solvent polarity, the present work endeavors to correlate and compare solvent and pressure effects on band maxima and intensities for the two electronic transitions.

Experimental Section

The six plastics that were used as solid "solvents" in the present work are listed in Table I along with macroscopic properties relevant to the present work. The numerical values do not have quantita-

Table I. Some Physical Properties of Polymer Matrices

Plastic	Abbrev	Density, ρ^a	$(\Delta V/V_0)_{10}$, kbar	Refractive index, n^a	Dielectric constant, D^a
Polyethylene	PE	0.86	0.09 ^b	1.51	2.25
Polystyrene	PS	1.05	0.12 ^c	1.59	2.45
Poly(methyl methacrylate)	PMMA	1.17	0.11 ^c	1.49	3.5
Cellulose acetate	CA	1.30	0.12 ^c	1.49	~ 4.7
Polyacrylonitrile	PAN	1.17	...	1.52	6.5
Poly(vinyl alcohol)	PVA	~ 1.25	0.06 ^b	1.51 ^d	...

^a "Modern Plastics Encyclopedia," Breskin Publications, Inc., New York, N. Y., 1963. ^b Reference 22b. ^c Reference 22a. ^d C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, p 351.

tive significance because they depend upon the precise history of preparation and treatment. For example, the properties of cellulose acetate (CA) depend upon the per cent acetylation (about 40%), and the polyethylene (PE) density is strongly affected by the average molecular weight. As the branching group becomes more polar, the density (ρ) and dielectric constant (D) increase, although the latter quantity is strongly reduced from that observed in monomer liquids. This is expected from its restricted motion, although the quantity applicable to the immediate environment of a solute molecule is probably considerably higher. The refractive index (n) is largest for polystyrene (PS) because of the phenyl groups, and for this plastic increases strongly in the spectral region of interest owing to the relatively long wavelength (~ 3000 Å) absorption of PS. Bridgman^{22a} and Weir^{22b} have reported the bulk compressibilities of several plastics, from which we extrapolate that the per cent volume contraction is practically the same except for the poly(vinyl alcohol) (PVA) plastic. This assumption permits the

comparison of spectral shifts and intensity changes in the various matrices at the same isobar. The absorption tail of the plastic does not extend below 3200 Å even at the highest pressures with the single exception of polystyrene.

The high-pressure absorption technique using a Cary Model 14 spectrophotometer has been reported.²³ The standard tungsten light source has been replaced with a halogen quartz lamp (Applied Physics Corp. accessory) which delivers sufficient intensities down to 3000 Å.

The chemical *trans*-azobenzene was purified on alumina columns. The plastic films, 0.010–0.030-in. thick, are prepared by evaporating suitable solvents containing azobenzene and dissolved polymer.²⁴ The concentrations are $\sim 3 \times 10^{-3}$ and ~ 0.2 M, respectively, for observing the π - π^* and n - π^* bands at an optical density ~ 1.5 .

The broad absorption bands are almost identical in plastic and liquid solutions of similar polarity, judging from their shape and maxima. In Table II the band maxima are reported for various media at normal pressure (1 atm). It is seen that the 317-m μ band (π - π^*) and the 445-m μ band (n - π^*) show a red and blue shift, respectively, in increasingly polar media. A molar extinction coefficient of 640 is computed for the n - π^* band of azobenzene in a CA film. The melting point, molar extinction, and exposure to ultraviolet radiation confirm the presence of only the *trans* isomer.

Table II. Maxima, Red Shift, and Intensity Ratios of Azobenzene Bands

	Band maxima (kK) at 1 atm		$-\Delta\nu$ (cm^{-1}) at 25 kbars		$I_{25\text{kbars}}/I_{1\text{atm}}$	
	π - π^* ^a	π - π^* ^b	π - π^* ^c	π - π^* ^d	π - π^*	π - π^*
Methylcyclohexane	22.4	31.5				
PE ^e	22.5	31.5	510	940	1.5	1.0
PS	22.5	31.15	450	...	1.8	...
PMMA	22.67	31.15	330	580	1.6	1.0
CA	22.7	31.25	260	660	1.3	1.0
PAN	22.8	30.86	420	750	1.2	1.0
PVA	22.8	30.86	-90	920	1.2	1.0

^a ± 100 cm^{-1} . ^b ± 150 cm^{-1} . ^c -50 cm^{-1} , +100 cm^{-1} . ^d ± 50 cm^{-1} . ^e See Table I for abbreviations.

Spectra taken with the sample in a solid holder and in the high-pressure optical cell at atmospheric pressure, corrected for the gently sloping base line, agree within 100 cm^{-1} for the two geometries. In every plastic at least three high-pressure runs were made for each band until two agreed within ± 50 cm^{-1} in the shift and ± 0.2 (n - π^* band) or ± 0.1 (π - π^* band) in the intensity ratios (I_P/I_{atm}) at 24 kbars for samples of identical concentration.

The intensity ratios have not been corrected for the small increase in the number of absorbing molecules at higher pressures, which is of little consequence for relative comparisons at a given isobar. Irreversible effects were not observed.

Results

The spectral distributions of the two absorption bands at atmospheric pressure and 25 kbars are compared in Figure 1. It is noted that the band shape retains its symmetrical character and shows very small or no broadening for the π - π^* and n - π^* bands, respectively, at higher pressures. This observation also holds true for the other plastics. The effects of pressures on the two absorption band maxima and their intensities are summarized in Table II for the 25-kbar isobar.²⁵ The red shifts at 25 kbars are larger for the π - π^* transition, although the comparatively weaker n - π^* band also shows a strong pressure dependence of the band maxima. Aside from the large shift in PE, the red shift increases steadily with increasingly polar functional groups on the polymer chain. The n - π^* band has

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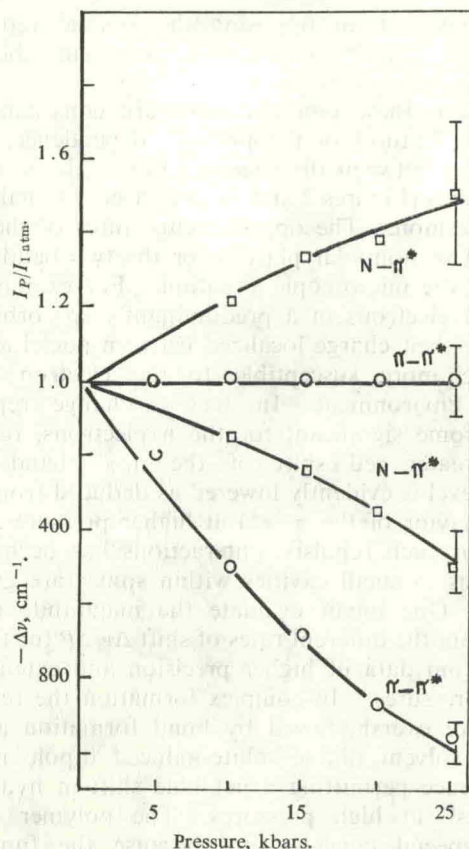


Figure 2. The effect of pressure on the intensities and band maxima of the π - π^* and n - π^* bands of azobenzene in polyethylene (PE).

larger displacements in nonpolar plastics and shows by comparison strong interactions opposing the red shifts in the plastics CA and PVA which are capable of hydrogen bonding. The n - π^* band maximum of azobenzene in PVA shows no displacement up to 20 kbars and then a small blue shift at 25 kbars. The intensity of the π - π^* band remains unchanged up to 25 kbars, within our experimental uncertainties. The intensity ratio increases very sharply for the weaker n - π^* band. Since the band width is nearly constant, the intensity ratio $I_p/I_{1\text{atm}}$ at the band maximum can be approximately set equal to the relative change in the theoretical absorption strength (f) of azobenzene. A nonpolar environment is more effective in increasing the transition probability. In this class of matrices, the large phenyl group (PS) is most influential in modifying the wave functions in the overlap region. It was found that the molar extinction of the n - π^* band in liquid solution (at 1 atm) increases with solvent polarity, while the pressure effect was largest in nonpolar plastics.

One reason that the azobenzene system was chosen for this comparative study of n - π^* and π - π^* bands was the fact that the two transitions are well separated in energy so that the contribution of the absorption edge of the strong band to the weak n - π^* band would be minimal. Extrapolation of the π - π^* absorption tail at atmospheric pressure shows that its contribution to the n - π^* band intensity at 445 $m\mu$ is negligible. However, the spectral shift of the π - π^* band is larger than in the n - π^* band so this fact contributes approximately 5–11% to the intensity ratio at the n - π^* band maximum at 25 kbars. In the case of PVA, the stronger

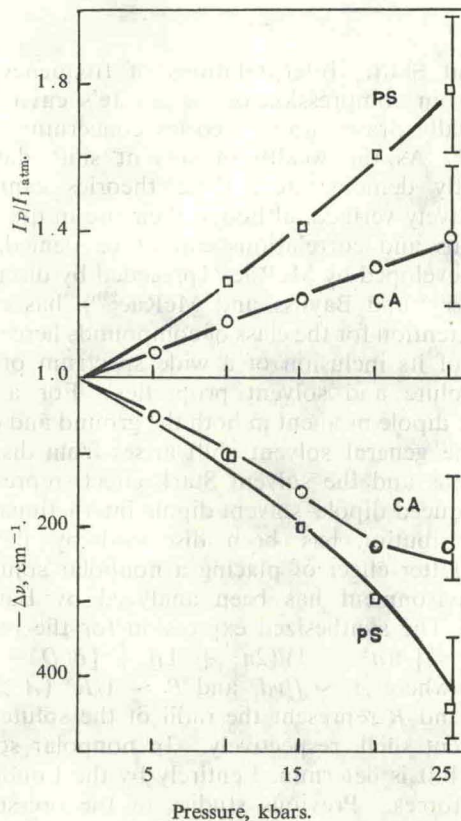


Figure 3. The effect of pressure on the n - π^* intensity and maximum of azobenzene in polystyrene (PS) and cellulose acetate (CA).

π - π^* band broadening makes an additional contribution at 25 kbars so that the blue shift would be larger than observed. This factor has not been included in the data (Table II) because the estimated correction factor lies within the stated uncertainty of the measurements. In Figures 2 and 3 the uncertainty has been indicated at 25 kbars. It is, of course, less at smaller pressures, but there exists an additional uncertainty in the pressure axis because of the quasihydrostatic pressure environment so that the cross-lines are left out for clarity below 25 kbars.

The contrast in the rate of change of $\Delta\nu$ and $I_p/I_{1\text{atm}}$ with pressure is demonstrated in Figure 2 for the PE matrix. The π - π^* band shows, as in the case of other π transitions in conjugated molecules,^{6,7} a curvature approaching the pressure axis. There is strong indication that the n - π^* transition shows a greater rate of shift $\Delta\nu/\Delta P$ in the highest pressure interval. This trend appears somewhat stronger in the PS matrix, as seen from Figure 3. The rate of shift of the n - π^* band in CA parallels that of PS to ~20 kbars and then appears to show a reversal at the highest pressure. As already mentioned, PVA shows no change to ~20 kbars and then a blue shift at 25 kbars. The same cause may be responsible for both observations. The intensity rise in the n - π^* band of azobenzene in PS appears to become steeper at higher pressures. These differences in $\Delta\nu/\Delta P$ are believed to be real, but their dependence on such parameters as changes of intermolecular distances requires smaller limits of error and the precise connection between compressibility and the applied pressure.

Discussion

Spectral Shift. Interpretations of frequency shifts arising from compression of the solute's environment have usually drawn upon theories concerning solvent shifts.^{10,26} As the wealth of solvent shift data has abundantly demonstrated, these theories cannot be quantitatively verified, although their use in qualitative predictions and correlations cannot be denied. One theory, developed by McRae²⁷ (preceded by discussions of Bayliss^{28a} and Bayliss and McRae^{28b}), has enjoyed special attention for the class of compounds here studied because of its inclusion of a wide spectrum of measurable solute and solvent properties. For a solute with zero dipole moment in both the ground and excited states, the general solvent shift arises from dispersive interactions and the solvent Stark effect, representing solute-induced dipole-solvent dipole interactions. The first contribution has been discussed by Bayliss,^{28a} and the latter effect of placing a nonpolar solute in a polar environment has been analyzed by Baur and Nicol.²⁹ The synthesized expression for the red shift is $-\Delta\nu = [A(n^2 - 1)/(2n^2 + 1)] + [B(D - 1)(2D + 1)/D]$ where $A \sim f/\nu d^3$ and $B \sim 1/R^3$ ($A \gg B$). Here, d and R represent the radii of the solute cavity and solvent shell, respectively. In nonpolar solvents, the red shift is determined entirely by the London dispersion forces. Previous studies of the pressure dependence of the band maxima of aromatic hydrocarbons^{6,7} suggest a linear decrease in cavity volume with increasing density so that the relative shift for two transitions should equal $f_1\nu_2/f_2\nu_1$. This ratio for the $\pi-\pi^*$ and $n-\pi^*$ bands is ~ 25 , while the ratio of the shift in PE at 25 kbars is ~ 2 . This poor agreement corresponds to that observed for the L_a and L_b bands of chrysene.⁶ The magnitude of the red shift in nonpolar solvents does not appear to discriminate between different types of electronic transitions. The red shift in polar solvents increases with increasing polarity, as expected from the Stark effect ($B > 0$). However, the least polar medium, PE, reveals the largest shift. Since the refractive index is about the same for all plastics (except PS), such discrepancy could be related to different compressibilities of the plastics or a larger solute cavity in the polar plastic.

The preceding discussion, based on general solvent shift theories, ignores the presence of specific interactions which can dominate environmental effects. The effect of hydrogen bonding of the azo group in PVA and CA plastics is definitely noticed in the observed spectral shifts of the $n-\pi^*$ band with increasing pressures. The blue-shift contribution in hydroxylic solvents can be attributed to a stronger hydrogen bond in the ground state which lowers the n orbital energy.^{20,21,30,31} This bond is considerably weakened upon promoting an n electron following light absorption. Increasing densities strengthen the hydrogen bond and form more complexes, including conceivably both sites in the molecule. The complex formation

contributes a term opposing the general red shift. This term appears to become dominant above 20 kbars.

Although these considerations are consistent with the gross features of the pressure dependence, subtle differences between the spectral shift of the $n-\pi^*$ and $\pi-\pi^*$ bands (Figures 2 and 3) cannot be rationalized in simple fashion. The opposite curvatures of the spectral shift in nonpolar plastics for the two bands must consider the microscopic situation. For example, the lone-pair electrons in a predominantly sp^2 orbital do not have their charge localized between nuclei and are therefore more susceptible to the electron clouds of the environment. In fact, exchange repulsion may become significant for the n electrons, resulting in a greater red shift of the $n-\pi^*$ band (since the π^* level is evidently lowered as deduced from pressure behavior of the $\pi-\pi^*$) at higher pressures. Evidence for such repulsive interactions has been found for atoms in small cavities within some rare gas matrices.³² One might evaluate the magnitude of this effect from the different rates of shift $\Delta\nu/\Delta P$ for the two bands from data of higher precision and extended to higher pressures. In complex formation the repulsive forces are overshadowed by bond formation and attractive solvent dipole-solute-induced dipole interactions, hence permitting a net blue shift in hydroxylic "solvents" at high pressures. The polymer PS requires special consideration because the functional group has relatively low energy levels capable of charge-transfer interaction with the solute. The degree of long-range order (per cent crystallinity) and the actual size of the groups on the polymer chain would also influence the size of the solute cavity, and, if the group is polar, further restrictions due to relative orientation restraints (solvent dipole- sp^2 -electron interactions) would be imposed. Other factors that may affect the spectral shift at higher densities include the n -orbital splitting, geometrical changes in the excited state, and electrostatic forces between the excited electron and the resultant hole, all of which could have a variable pressure dependence, which cannot be expressed in terms of solvent bulk properties.

Intensities. In contrast to solvent shifts, the problem of intensities is seldom mentioned because it is difficult to evaluate the distortion of the charge distribution in the two electronic states when intermolecular interactions are modified by solvents or pressure. Attempts to correct the transition moment integral by the correction factor $(n^2 + 2)^2/9n^{33}$ upon passing from the vapor to solution have been discarded.³⁴

The results clearly show a great difference between the pressure behavior of the two bands. In agreement with π systems (aromatics), the maximum intensity is largely unaffected by pressure. The increase in band width appears smaller for the "localized" $\pi-\pi^*$ transition in azobenzene in comparison with transitions in highly conjugated π systems. Hence, there is little change in absorption strength upon compression for π excitation. However, the $n-\pi^*$ is significantly enhanced at higher densities. This sensitivity to external perturbation must be related to the relaxation

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of the symmetry-forbiddenness or an increased effectiveness in intensity-stealing from the color band.^{16, 18} The compression of a crystal should show evidence of out-of-plane polarization, but this experiment has not been performed. It might be expected that a weak transition is more easily perturbed and that the local symmetry could be distorted by the closer proximity of the solvent electrons or the simultaneous excitation of antisymmetric vibrations.

It has been argued that the diffuse character of the $n-\pi^*$ band arises from strong mixing with the color band.^{15, 16, 18} Such mixing is enhanced by decreasing the separation of the two states, which is indeed the

result of external pressure application since $\nu_{\pi\pi^*}(P) > \nu_{n\pi^*}(P)$. However, the pressure dependence of $1/\Delta E$ cannot be the largest factor determining intensity changes because ΔE is the smallest in PVA at 25 kbars, and yet its intensity rises less than in the other plastics. Hence, increases in the interaction matrix must make a sizable contribution at high pressures.

The precise source of the greater intensity in a strongly perturbed environment cannot be determined from the present information which nevertheless demonstrates the magnitude of the differences in the pressure behavior of localized $\pi-\pi^*$ and $n-\pi^*$ transitions in the same molecule.