# Polar and Hydrogen-Bonding Interactions in Supercritical Fluids. Effects on the Tautomeric Equilibrium of 4-(Phenylazo)-1-naphthol

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The azo-hydrazone tautomeric equilibrium of 4-(phenylazo)-1-naphthol is compared in various liquid and supercritical fluid solvents. The less polar azo tautomer is dominant in the dilute gas phase, compressed ethane, and liquid alkanes. In liquid and supercritical  $CO_2$ , the equilibrium shifts toward the more polar hydrazone, to yield similar amounts of the two tautomers. This shift is attributed to the Lewis acidity and large quadrupole moment of CO<sub>2</sub>. The dominance of the hydrazone tautomer in fluoroform (>90%) can be attributed to that solvent's large dipole moment and ability to act as a strong electron acceptor (hydrogen bond donor). Since acid-base interactions are prevalent at the lowest pressure studied (1000 psia), changes in the equilibrium constant as a function of pressure have been assigned primarily to increases in the nonspecific polar interactions. The large differences in the polarities, acidities, and basicities of these fluids, despite their similar polarizabilities per volume, are of interest for manipulating chemical processes and for practical applications of supercritical fluid science and technology.

### Introduction

The properties of a single supercritical fluid (SCF) such as density, dielectric constant, and solubility parameter can be altered between gas- and liquidlike extremes through modest manipulations of pressure and/or temperature. This causes large changes in the chemical potential of a solute, as described by pronounced partial molar volumes and enthalpies.<sup>1</sup> This adjustability of the solvent strength is the basis for supercritical fluid extraction<sup>2</sup> and chromatography.<sup>3</sup> More recently, supercritical fluids have been used to adjust rate constants<sup>4,5</sup> and selectivities<sup>6</sup> of chemical reactions and for chemical synthesis.7 To understand the effect of pressure on both reaction and separation processes in supercritical fluids, a more thorough characterization of the nature and extent of solvent-solute interactions is required.

The interactions between a solute and a pure supercritical fluid have been characterized at the molecular level with UV-visible and fluorescence indicators<sup>8-10</sup> and by computer simulation.<sup>11</sup> Most of these studies have focused on manipulating nonspecific solute-solvent interactions by changing the fluid's solubility parameter or polarizability per unit volume, and thus, very little is known about polar and specific forces, e.g., acid-base interactions. The Lewis acidity of fluoroform has been characterized with the solvatochromic probe phenol blue.8 The acid-base interactions were well-developed at 1000 psia and did not change significantly with pressure. The Lewis acidity and basicity of  $CO_2$  have also been measured with IR spectroscopy, based on its interactions with pyrrole and ketones.<sup>12</sup> A related problem, the hydrogen bonding between a solute and a cosolvent, or between two solutes, is of continuing interest<sup>13-15</sup> and will not be discussed.

In general, the strength of specific interactions between a solute and a supercritical fluid has been inferred from its solubility.13 Unfortunately, there are a number of difficulties associated with this approach. Often the volatility of the solute is extremely low, and the vapor pressure is known inaccurately or not at all. This severely limits the determination of the nonidealities in the fluid phase. The differentiation of the effects caused by solute-solvent repulsive forces and those caused by the attractive forces introduces uncertainty. Another difficulty is the resolution of the relative importance of the van der Waals, polar, and hydrogen-bonding interactions, all which are known to significantly influence solubility. Clearly, other complementary approaches are needed.

To focus attention on hydrogen-bonding and polar interactions, we have chosen to investigate the equilibrium between the azo and hydrazone tautomers of 4-(phenylazo)-1-naphthol (eq 1). The equilibrium is influenced strongly by the properties of the solvent, because of the large differences in the dipole moments and electron

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donor and acceptor (hydrogen-bonding ability) properties of each tautomer.<sup>16</sup> This tautomerization is a good candidate for highpressure experimental study as it may be monitored in situ by UV-visible spectrophotometry near infinite dilution.

By studying molecular interactions with a reversible chemical

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	dipole moment, <sup>a</sup> D	polarizability/ volume <sup>b</sup>	solvent polarity parameters <sup>c,d</sup>				equilibrium
solvent			π	β	α	$\overline{E_t(30)}$	constant, K <sub>c</sub>
acetone	2.9	0.052	0.71	0.48	0.08	42.2	0.43
benzene	0	0.070	0.59	0.1	0	34.3	1.27
chloroform	1.1	0.061	0.58	0	0.44		3.76
<i>n</i> -hexane	0	0.054	-0.08	0	0	31.0	
methanol	1.7	0.048	0.6	0.62	0.93	55.4	0.67
	solvent	dipole moment, <sup>a</sup> D	quadrupole moment, <sup><math>f</math></sup> 10 <sup>26</sup> erg <sup>1/2</sup> cm <sup>5/2</sup>		critical temp, <sup>a</sup> °C	critical press., <sup>a</sup> psia	
	carbon dioxide	0	-4.3		31	1070	
	ethane	0	-0.65		32	708	
fluoroform benzene		1.6			26	7	/05
		0	3.6		289	709	

TABLE I: Solvent Properties and Polarity Parameters of Various Solvents

<sup>a</sup> Taken from ref 23. <sup>b</sup> The  $\alpha/v$  values have been multiplied by Avogadro's number to make them dimensionless, ref 24. <sup>c</sup> Kamlet-Taft constants, ref 25, where  $\pi$  is a measure of dipolarity and polarizability,  $\beta$  is a measure of hydrogen-bond acceptor basicity, and  $\alpha$  is a measure of hydrogen-bond donor acidity. <sup>d</sup> The  $E_1(30)$  value is the  $\pi$  to  $\pi^*$  transition energy, in kcal/mol, for the longest wavelength absorption band of pyridinium N-phenoxide betine dye; for a more complete explanation set ref 19, pp 365-371. <sup>c</sup>Taken from ref 16b. <sup>f</sup> From ref 26.

process instead of solubility phenomena, several difficulties are ameliorated. For example, it is not necessary to know solute vapor pressures. Since the tautomers have very similar sizes, solutesolvent repulsive forces should have little effect on the equilibrium constant,  $K_c = [hydrazone]/[azo]$ . Therefore, observed changes in  $K_c$  with pressure can be attributed to changes in the attractive molecular interactions between each tautomer and the fluid. (Notice that Le Chatelier's principle predicts that pressure would not shift the equilibrium since the stoichiometric coefficient of each tautomer is unity.) Because the polarizabilities of the tautomers are similar, the effect of van der Waals forces on  $K_c$  is minor, and it is possible to focus nearly exclusively on polar (dipole-dipole, dipole-induced dipole, dipole-quadrupole) and hydrogen-bonding interactions. In this work we report the effects of pressure on the tautomeric equilibrium of 4-(phenylazo)-1naphthol in several supercritical fluids, ethane, CO<sub>2</sub>, and fluoroform. The results provide valuable information about the fundamental nature and the strength of polar and hydrogenbonding interactions between these tautomers and several supercritical fluids.

# **Experimental Section**

**Materials.** 4-(Phenylazo)-1-naphthol was synthesized by the method of Kishimoto et al.<sup>17</sup> Recrystallization from a 4:1 water:acetone mixture yields a brown solid: mp 209–211 °C (lit.<sup>18</sup> 205–206 °C). The identity of the reaction product was confirmed by UV-vis, NMR, and mass spectrometry. CO<sub>2</sub> (Liquid Carbonic, 99.99% purity) and ethane (Big Three Gases, CP grade) were used as received. Fluoroform (Linde Halocarbon 23, 98% purity) was purified by passing it through activated carbon.

Equipment. A 6 cm path length spectroscopic cell (14.3-mL volume) was made of stainless steel with two sapphire windows (2.5-cm diameter, 1.0-cm thickness). Two cartridge heaters (Gaumer, 6 in., 120 V, 125 W), a platinum resistance thermometer (Omega), and an RTD temperature controller (Omega) were used to regulate the temperature. A syringe pump (High Pressure Equipment, 60-mL capacity) was used to load solvent and control the pressure which was monitored with a digital pressure transducer (Autoclave,  $\pm 20$  psia accuracy). Absorbance values were measured to a wavelength accuracy of  $\pm 0.2$  nm with a Varian (Cary) 2290 UV-visible spectrometer. The typical reproducibility in the ratio of absorbances for the tautomers was 5%.

**Procedure.** A measured amount of a 4-(phenylazo)-1-naphthol in acetone solution was loaded into the spectroscopy cell, and the acetone was evaporated with a nitrogen purge. After purging the air from the cell with low-pressure solvent gas, the cell was pressurized as desired. The resulting fluid mixture was stirred for >1/2 h with a 1-cm magnetic stir bar. Spectra were measured sequentially, always in the order of increasing pressure. Since



Figure 1. UV-visible spectra of 4-(phenylazo)-1-naphthol in benzene, methanol, acetone, and chloroform (path length = 1 cm; concentration =  $3.2 \times 10^{-5}$  M).

neither solvent gas nor solute was allowed to escape from the cell, a constant molar concentration was maintained. A spectrum of the pure solvent in the cell was used as the baseline.

## **Results and Discussion**

Liquid Solvents. As a control, the tautomerization was studied in several liquid solvents. The tautomeric equilibrium of 4-(phenylazo)-1-naphthol (eq 1) is strongly solvent dependent.<sup>16</sup> Calculations suggest the azo tautomer will dominate in the gas phase.<sup>19</sup> Nonpolar solvents, such as hexane, shift the equilibrium slightly toward the more polar hydrazone tautomer (via dipoleinduced dipole interactions), but the equilibrium is dominated by the azo form. The hydrazone tautomer, which has the larger dipole moment, is stabilized by polar solvents. While electron-donating solvents, such as pyridine, stabilize the azo form through interactions with the hydroxyl group, electron-accepting solvents, such as acetic acid, shift the equilibrium toward the hydrazone tautomer.<sup>16</sup>

Figure 1 shows the UV-visible spectra of 4-(phenylazo)-1naphthol in several liquid solvents. The absorption maximum at  $\sim$ 400 nm is assigned to the azo tautomer, while that at  $\sim$ 465 nm is assigned to the hydrazone. These results may be interpreted with the solvent physical properties listed in Table I.

The interpretation is more complicated in polar solvents which possess the ability to hydrogen bond, such as acetone, chloroform, and benzene. In benzene, the equilibrium shifts toward the hydrazone species, relative to hexane, because of the larger polarizability per volume,  $\alpha/v$ , and quadrupole moment for benzene. Apparently the slight Lewis basicity of benzene, which would

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Figure 2. Spectra in ethane (24 °C, 2000 psia,  $3.0 \times 10^{-6}$  M):  $\Box$ , experimentally measured spectrum;  $\blacktriangle$ , deconvoluted azo spectrum;  $\bullet$ , deconvoluted hydrazone spectrum; —, sum of deconvoluted azo and hydrazone spectra.

stabilize the azo form, has little effect compared with the dipole-quadrupole and dipole-induced dipole forces. The angleaveraged dipole-induced dipole and dipole-quadrupole potentials may be expressed as

$$\Gamma_{ii}$$
(dipole-induced dipole) =  $-\alpha_i \mu_i^2 / r^6$  (2)

$$\Gamma_{ii}(\text{dipole-quadrupole}) = -Q_i^2 \mu_j^2 / r^8 kT$$
(3)

where  $\Gamma_{ij}$  is the interaction energy between molecules *i* and *j*,  $\alpha_i$  is the polarizability,  $\mu_j$  is the dipole moment, and *Q* is the quadrupole moment.<sup>20</sup> Although the large dipole moment (2.8 D) of acetone should stabilize the more polar hydrazone tautomer, hydrogen bonding dominates the electrostatic forces and the azo form is dominant. The different results in benzene and acetone are consistent with the much larger Lewis basicity of acetone. In chloroform, a hydrogen bond donor, the equilibrium is shifted strongly toward the hydrazone tautomer. Because of these large solvent effects for both hydrogen bond donors and acceptors, this tautomerization process is useful for probing the hydrogen-bonding abilities of supercritical fluids.

In order to determine the equilibrium constant,  $K_c$ , quantitatively from the spectra, the absorbance of each tautomer is required. Since the peaks of the two tautomers overlap, a deconvolution method was developed. The spectral curves of the two tautomers were assumed to be Gaussian with equal variances. A computer routine was used to optimize the locations, heights, and variance of the two tautomer peaks, so that the sum of the deconvoluted peaks most accurately fit the experimental spectra. In general, the deconvolution method was only used when the average absorbance was above 0.05 in order to minimize the uncertainty and error associated with the manipulation. The equilibrium constant defined by

$$K_{\rm c} = [\rm hydrazone] / [\rm azo]$$
 (4)

may be determined from the resolved spectra. Application of Beer's law yields

$$K_{\rm c} = \frac{A(\rm hydrazone)}{A(\rm azo)} \frac{\epsilon(\rm azo)}{\epsilon(\rm hydrazone)}$$
(5)

Note that this value is independent of total concentration. The determination of each individual extinction coefficient is complicated by the presence of both tautomers at equilibrium. The equilibrium constants were 0.76, 0.49, 1.33, and 3.13 in methanol, acetone, benzene, and chloroform, using the ratio of extinction coefficients determined from chemical analogues in each solvent, which do not tautomerize.<sup>16b</sup> These results are on average within about  $\pm 12\%$  of those reported previously. Because the ratio of extinction coefficients for the chemical analogues varied little among these solvents, we assume that it will also not vary ap-



Figure 3. Spectra of 4-(phenylazo)-1-naphthol in (a) hexane (24 °C, 15 psia) and ethane (24 °C, 3100 psia,  $3.0 \times 10^{-6}$  M), (b) benzene (24 °C, 15 psia,  $3.2 \times 10^{-5}$  M) and carbon dioxide (24 °C, 2040 psia,  $5.0 \times 10^{-6}$  M), and (c) chloroform (24 °C, 15 psia,  $3.2 \times 10^{-5}$  M) and fluoroform (24 °C, 2950 psia,  $3.4 \times 10^{-6}$  M).  $\Box$ , left axis;  $\bullet$ , right axis.



Figure 4. Ratio of hydrazone/azo tautomer peak heights versus pressure in carbon dioxide and ethane:  $\blacktriangle$ ,  $5.0 \times 10^{-6}$  M;  $\square$ ,  $1.5 \times 10^{-5}$  M;  $\bigcirc$ ,  $5.0 \times 10^{-6}$  M;  $\triangle$ ,  $2.5 \times 10^{-6}$  M;  $\blacksquare$ ,  $3.0 \times 10^{-6}$  M.

preciably for the supercritical fluids.

Ethane. The experimental and deconvoluted spectra for 4-(phenylazo)-1-naphthol in ethane are shown in Figure 2. The spectra in ethane at 22 °C and 3100 psia and in liquid hexane at ambient pressure are very similar with the azo tautomer being dominant (Figure 3a). The values of  $K_c$  are approximately equal, given  $\epsilon(azo)/\epsilon(hydrazone)$  is similar for the two solvents. The similarity in the solvent characteristics of hexane and ethane has also been observed for UV-visible and fluorescence probes.<sup>9,10</sup>

The  $K_c$  of 4-(phenylazo)-1-naphthol in subcritical liquid ethane does not appear to vary significantly with pressure at 22 °C from 1000 to 3100 psia (Figure 4). The changes in  $K_c$  with pressure may be determined from eq 5, assuming that the ratio  $\epsilon(azo)/\epsilon$ (hydrazone) does not change. Since the molar volume undergoes only a small change,  $\alpha/v$  varies by only 20%, the equilibrium is not shifted significantly toward the hydrazone species (Figure 5). If the density and  $\alpha/v$  of supercritical ethane (temperatures above 32 °C) were decreased by more than a factor of 2, this would be expected to influence  $K_c$  significantly because of the differences in the strengths of the dipole-induced dipole interactions between each tautomer and the solvent.<sup>5</sup> In the reversible tautomerization



Figure 5. Polarizability per unit volume versus pressure for carbon dioxide (25 and 35 °C), ethane (22 °C), and fluoroform (22 °C).

of 2-hydroxypyridine and 2-pyridone at infinite dilution, the partial molar volume change on reaction reached -1400 mL/mol near the critical point of the solvent. Unfortunately, the solubility of 4-(phenylazo)-1-naphthol was too low at lower densities to obtain spectra, even with the 6 cm path length cell.

**Carbon Dioxide.** In many cases  $CO_2$  and ethane behave similarly as supercritical fluid solvents, although in some instances there are interesting differences. The unusually high critical pressure of  $CO_2$  versus ethane is due in part to the large quadrupole moment of  $CO_2$ . Perturbation theory predicts that the large quadrupole moment associated with  $CO_2$  will influence the solubilities of polar solutes.<sup>21</sup> The reversible chemical reaction between  $CO_2$  and ammonia or amines to form carbamates nicely demonstrates the electron-accepting ability of  $CO_2$ . Finally, an unexplained observation of great interest is that reverse micelles and microemulsions may be formed with various surfactants in ethane and ethylene, but not in  $CO_2$ .<sup>22</sup> The quadrupole moment or the acidity of  $CO_2$  likely plays a role in this unexplained observation. The understanding of these observations could be improved given a fundamental description of the polarity and acidity of  $CO_2$  as a supercritical fluid.

The spectra of 4-(phenylazo)-1-naphthol in CO<sub>2</sub> were measured at different concentrations to determine the solubility and to ensure adherence to Beer's law (see Figure 4). Although the extinction coefficients change modestly with pressure,  $\sim 2\%/100$  psia, we assume that the ratio of the extinction coefficients remains constant. The fact that pressure can influence extinction coefficients in supercritical fluids must be considered in quantitative analysis, for example, in supercritical fluid chromatography.

Although the  $\alpha/v$  of CO<sub>2</sub> is similar to that of ethane (see Figure 5), CO<sub>2</sub> causes a large shift in the equilibrium toward the more polar hydrazone tautomer, analogous to benzene (Figure 3b). This observation is consistent with the  $E_t(30)$  parameters, an empirical measure of solvent polarity,<sup>19</sup> for subcritical and supercritical CO<sub>2</sub> reported by Hyatt.<sup>12</sup> His results showed CO<sub>2</sub> ( $E_t(30) = 33.8$  kcal/mol at 1000 psia, 24 °C) to have a polarity close to benzene and toluene but significantly higher than those of aliphatic hydrocarbons (*n*-pentane, 31.0; *n*-hexane, 31.0). The higher polarity of CO<sub>2</sub> may be attributed to the sensitivity of  $E_t(30)$  to Lewis acids.

The deconvoluted spectra in Figure 6 indicate that nearly equal amounts of the tautomers are present in  $CO_2$ . If only dipole-

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**Figure 6.** Spectra of 4-(phenylazo)-1-naphthol in carbon dioxide (35 °C, 3932 psia,  $1.5 \times 10^{-5}$  M):  $\Box$ , experimentally measured spectra;  $\blacktriangle$ , deconvoluted azo spectra;  $\blacklozenge$ , deconvoluted hydrazone spectra; —, sum of deconvoluted azo and hydrazone spectra.



**Figure 7.** Difference in polar (dipole-induced dipole and dipole-quadrupole) contributions to the pair potential,  $\Delta \Gamma_{ij}{}^p = \Gamma_{ij}{}^p$ (hydrazone) –  $\Gamma_{ij}{}^p$ (azo).

induced dipole forces were present, similar results may be expected for CO<sub>2</sub>, ethane, and ethylene, since all three have similar values of  $\alpha/v$ . This analysis is supported by solvatochromic studies in nonpolar supercritical fluids, for  $E_1$  of phenol blue,<sup>8</sup> which showed similar shifts in CO<sub>2</sub> and ethylene at constant density.

Clearly, the shift in  $K_c$  toward the more polar and basic tautomer, hydrazone, in CO<sub>2</sub> relative to ethane must be due to other types of interactions. This shift is consistent with the much larger quadrupole moment for CO<sub>2</sub>, as was the case for liquid benzene. In addition, the Lewis acidity of CO<sub>2</sub> should also stabilize the hydrazone tautomer. In order to distinguish between the effects of the quadrupole moment and acidity, it is instructive to examine the pressure effect on  $K_c$ , solvent effects on  $K_c$  in other liquids and fluids, and other spectroscopic data in supercritical CO<sub>2</sub>.

The primary difference between specific forces and polar forces is that specific forces become saturated, even at low pressures, whereas polar forces do not. This concept may be expected from statistical mechanical perturbation theory<sup>11,13</sup> and has been studied for the solvatochromic indicator phenol blue in supercritical fluoroform.<sup>8</sup> In the latter study, the shift due to the hydrogen bond was already evident at 730 psia and does not change significantly over a wide range of pressures, up to 4400 psia. Since only one or two solvent molecules are required to form a hydrogen bond, it is not surprising that hydrogen bonds could be formed at relatively low pressures and densities. Once they are formed, an increase in pressure does not appear to have a large influence on the hydrogen-bonding strength. In contrast, as pressure increases, the nonspecific forces become stronger as the number of solvent molecules about the solute increases, and the distance between molecules decreases. The pressure-induced shifts in  $K_c$ for 4-(phenylazo)-1-naphthol are consistent with this concept (Figure 4). The shifts with pressure appear to be influenced more strongly by dipole-quadrupole interactions than by acid/base interactions.

In order to examine the pressure effect further, we consider the change in the solute-solvent pair potential as a function of

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Figure 8. UV-visible spectra of 4-(phenylazo)-1-naphthol in carbon dioxide at 25 and 35 °C ( $5 \times 10^{-6}$  M).

the intermolecular separation, r, between the solute and solvent molecules. The effect of the decrease in r is shown in Figure 7 in a plot of the difference in the polar contributions to the pair potentials

$$\Delta \Gamma^{p} = \Gamma_{ij}^{p}(\text{hydrazone}) - \Gamma_{ij}^{p}(\text{azo})$$
(6)

where

$$\Gamma_{ij}{}^{p} = \Gamma_{ij}(\text{dipole-induced dipole}) + \Gamma_{ij}(\text{dipole-quadrupole})$$
(7)

In all cases,  $\Delta \Gamma^{p}$  is negative due to the larger  $\mu$  for the hydrazone tautomer. As *r* decreases, the magnitudes of the energy differences increase faster for CO<sub>2</sub> and benzene than ethane as a result of their larger quadrupole moments. This increase in the difference in polar interactions,  $\Delta \Gamma^{p}$ , is likely a primary cause for the shift in  $K_{c}$  with pressure.

The intermolecular forces may be characterized further by examining the effect of temperature on  $K_c$ . The temperature effect on a reversible reaction is given by

$$d \ln K_a / dT = \Delta H^o / RT^2$$
(8)

where  $K_a$  is the equilibrium constant based on activity and  $\Delta H^o$  is the standard molar enthalpy change on reaction. For an ideal gas standard state at unit pressure, the standard state fugacities are unity and

$$K_{\rm a} = y_2 \phi_2 / y_1 \phi_1 \tag{9}$$

where  $y_1$  and  $\phi_1$  are the molar fraction and fugacity coefficient (equal to unity in an ideal gas) of the reactant and similarly for the product, species 2. An equivalent expression is

$$K_{\rm a} = K_{\rm c}(\phi_2/\phi_1) \tag{10}$$

Equations 8 and 10 may be combined with the expression

$$(\partial \ln \phi_i / \partial T)_p = (H_i^\circ - \bar{H}_i) / RT^2$$
(11)

where  $H_i^{\circ}$  and  $\tilde{H}_i$  are the standard state molar enthalpy and partial molar enthalpy for each species, i = 1, 2 to yield

$$(\partial \ln K_c / \partial T)_p = (\bar{H}_2 - \bar{H}_1) / RT^2$$
 (12)

The equilibrium shifts toward the azo tautomer with increasing

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temperature in the inert solvent methylcyclohexane.<sup>16e</sup> The same is true for  $CO_2$  (Figure 8), which establishes that the enthalpic interactions are stronger between  $CO_2$  and the hydrazone than with the azo form, presumably because of different electron-accepting ability and dipole-quadrupole interactions. A similar result was observed for the tautomerization of 2-hydroxypyridine in propane.<sup>5</sup> The solute-solvent enthalpic interactions were stronger with the more polar tautomer, because of the dipole-induced dipole interactions. Near the critical point of the solvent where the volume expansivity is large, it was calculated that the partial molar enthalpy change on tautomerization of 2-hydroxypyridine reaches -170 kJ/mol.

**Fluoroform.** As shown in Figure 3c, the equilibrium in fluoroform is shifted far toward the hydrazone form. This large shift toward the hydrazone form relative to that observed in  $CO_2$  is consistent with the strong Lewis acidity of fluoroform and dipole-dipole interactions which are not present for  $CO_2$ . The spectra in fluoroform (23 °C, 2950 psia) and chloroform at ambient pressure are similar, suggesting similar Lewis acidities. Similar results were found for fluoroform and chloroform in solvatochromic studies with phenol blue.<sup>8</sup>

In fluoroform, a small azo concentration is apparent at lower pressures. As pressure increases above 1500 psia, the equilibrium shifts even more toward the hydrazone form, and the uncertainty in the azo concentration increases. The calculated hydrazone-to-azo ratios were 2.0, 2.5, and 2.7 at pressures of 1002, 1590, and 2950 psia and room temperature. On the basis of the above arguments for  $CO_2$ , it is probable that the shift in  $K_c$  with pressure is due primarily to increases the polar interactions and that the effect of hydrogen bonding is relatively constant.

#### Conclusions

The polarizabilities per unit volume of supercritical fluid solvents with critical temperatures near 25 °C are similar. Therefore, the strengths of solute-solvent interactions are similar for nonpolar solutes in CO<sub>2</sub>, ethane, and fluoroform, as seen in previous studies of solubilities and solvatochromic shifts.<sup>9</sup> However, the results from this study of the tautomeric equilibria of 4-(phenylazo)-1naphthol indicate that ethane, CO<sub>2</sub>, and fluoroform have extremely different characteristics as solvents because of differences in polar interactions and hydrogen bonding. As in a previous study,<sup>8</sup> hydrogen bonding can be well-developed in CO<sub>2</sub> and fluoroform at 1000 psia and changes less than that of polar interactions as pressure is increased to 4000 psia. This fundamental understanding of polar and specific interactions is useful for interpreting the behavior of interactions between solutes and supercritical fluids in extraction, chromatography, and chemical reactions.

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**Registry No.** CO<sub>2</sub>, 124-38-9; 4-(phenylazo)-1-naphthol, 3651-02-3; acetone, 67-64-1; benzene, 71-43-2; chloroform, 67-66-3; *n*-hexane, 110-54-3; methanol, 67-56-1; ethane, 74-84-0; fluoroform, 75-46-7.