

Least-squares refinements minimized the function $\sum_{hkl} w(F_0 - F_c)^2$ where the weighting factor was $w = 1/\sigma(F_0)^2$. All hydrogen atoms were located in a difference Fourier map. The largest peak in the final difference Fourier map showed $0.062 \text{ e}\cdot\text{\AA}^{-3}$ near O1. Full-matrix least-squares refinement with anisotropic thermal parameters for 17 carbon and oxygen atoms, and isotropic thermal parameters for 10 hydrogen atoms, led to $R = 5.7\%$, $R_w = 6.9\%$, maximum $\Delta/\sigma = 0.35$ (x of H1), with 195 variables. Additional crystallographic details are presented in the supplementary material.

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Supplementary Material Available: Listings of crystal structure data, positional and thermal parameters, bond distances and angles, least-squares planes, torsion angles, and experimental and calculated structure factors for the structure of 1 (21 pages). Ordering information is given on any current masthead page.

Perturbations of an Isotopically Substituted Nonhydroxylic Solvent upon the Chemistry of an Anion Radical

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Introduction

There have been a number of studies on the effect of the replacement of hydrogen with deuterium upon acidity and basicity, and the results show that deuterium behaves as though it were electron donating relative to hydrogen.¹ This behavior is responsible for a number of observed solvent isotope effects.² Most reports of solvent isotope effects have involved kinetic studies where water/deuterated water or other hydroxylic solvents served as the solvent systems.³ We wish to report an equilibrium isotope effect from a nonhydroxylic solvent that is consistent with the electron-releasing nature of deuterium. EPR evidence indicates that the perdeuteriation of the most common anion radical solvent, tetrahydrofuran (THF), measurably increases its ability to separate ions involved in ion-pairing equilibria.

When naphthalene dissolved in THF is exposed to a freshly distilled sodium mirror under vacuum, the solvated anion radical ($\text{C}_{10}\text{H}_8^{\cdot-}$) is generated and exists in at least three different states of ion association. These include the free solvated ion ($\text{C}_{10}\text{H}_8^{\cdot-} + \text{Na}^+$)^{4a} as well as the sol-

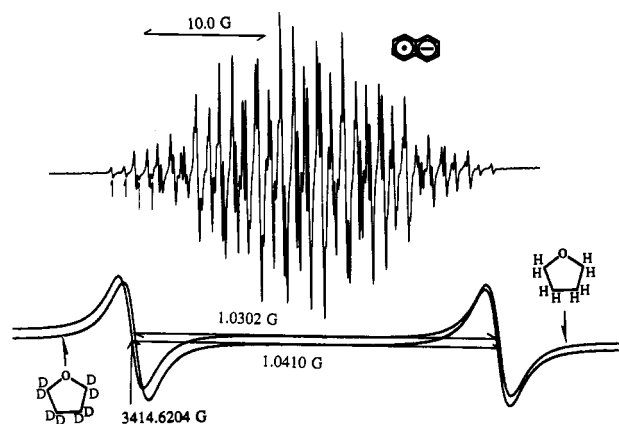
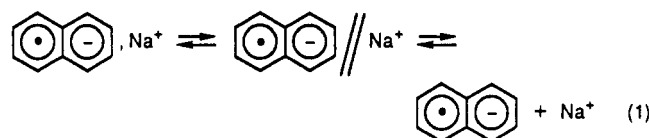


Figure 1. (Top) EPR spectrum of the sodium salt of the naphthalene anion radical in THF- d_8 at 298 K. The vertical arrows mark the low-field quartet due to the sodium splitting. (Bottom) computer simulations of the first two lines of the spectrum using the average of the field positions (marked for first line) for each line as measured with the Gaussmeter. Note that both lines recorded from the sample in THF lie outside of those for the sample in THF- d_8 .

vent-separated ($\text{C}_{10}\text{H}_8^{\cdot-}/\text{Na}^+$) and contact ion pairs ($\text{C}_{10}\text{H}_8^{\cdot-}, \text{Na}^+$) first reported by Zandstra and Weissman.^{4b} Upon EPR analysis, the resulting solution exhibits an averaged sodium hyperfine splitting ($A_{\text{Na}} = 1.03 \text{ G}$) at 28 °C (see Figure 2 in ref 4b). This observed splitting is controlled by the overall degree of ion association between the anion radical and the sodium cation, reaction 1,⁴ and



is a time or weighted average of those for the solvated tight or contact ion pair ($A_{\text{Na}^{\text{t}}}$), the solvent-separated ion pair ($A_{\text{Na}^{\text{s}}}$), and the free solvated ion ($A_{\text{Na}^{\text{f}}}$), eq 2.^{4c,5} The

$$A_{\text{Na}} = (A_{\text{Na}^{\text{t}}}[\text{C}_{10}\text{H}_8^{\cdot-}, \text{Na}^+] + A_{\text{Na}^{\text{s}}}[\text{C}_{10}\text{H}_8^{\cdot-}/\text{Na}^+] + A_{\text{Na}^{\text{f}}}[\text{C}_{10}\text{H}_8^{\cdot-} + \text{Na}^+]) / ([\text{C}_{10}\text{H}_8^{\cdot-} + \text{Na}^+] + [\text{C}_{10}\text{H}_8^{\cdot-}, \text{Na}^+] + [\text{C}_{10}\text{H}_8^{\cdot-}/\text{Na}^+]) \quad (2)$$

coupling constant for the free ion is zero, and that for the solvent-separated ion pair also appears to be near zero, while that for the contact ion pair is reported to be larger than 1.5 G.^{4c}

Results and Discussion

Exposure of naphthalene solutions in perdeuteriated THF (THF- d_8) to a freshly distilled sodium mirror under high vacuum leads to anion radical solutions that yield the typical 100-line EPR pattern at room temperature (splitting from 4 β and 4 α protons and 1 Na) or 25 line pattern at -100 °C (no sodium splitting). Careful recordings (sweep widths of 1.2 and 1.4 G) taken within a few minutes to a few days of sample preparation of the low-field portion of the EPR spectrum of sodium naphthalene anion radical at 298 K reveal that the sodium splitting (A_{Na}) is smaller for samples dissolved in THF- d_8 than it is for those samples generated in normal THF (Figure 1). Samples of the naphthalene anion radical were generated using identical techniques in THF and in THF- d_8 . A sample in THF was placed in the front cavity

(1) (a) A single deuterium will split the degeneracy of the antibonding MO's of benzene as does an electron-releasing group; see: Alper, J. S.; Silby, R. *J. Chem. Phys.* 1970, 52, 569. Stevenson, G. R.; Reidy, K. A.; Peters, S. J.; Reiter, R. C. *J. Am. Chem. Soc.* 1989, 111, 6578. (b) The electrochemical reduction potential of deuterated polyaromatics is more negative than those of their light isotopic analogues; see: Goodnow, T. T.; Kaifer, A. E. *J. Phys. Chem.* 1990, 94, 7682. See also: (c) Bary, Y.; Gilboa, H.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* 1979, 938. (d) Srinivasan, R.; Stewart, R. *J. Am. Chem. Soc.* 1976, 98, 7648.

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and a sample in THF- d_8 in the back cavity of a dual cavity EPR spectrometer, after which the first two lines of each spectra were recorded (Figure 1). The sample positions were then interchanged and the spectra again recorded. For all samples, it was observed that the distance between the first line of the spectrum (an $m = -3/2$ from the sodium splitting) to the second line (an $m = -1/2$) is slightly smaller when the deuterated solvent replaced the normal THF. On the basis of more than 50 such measurements involving a number of different solutions, it was found that ΔA_{Na} (A_{Na} in THF minus A_{Na} in THF- d_8) is 10.7 ± 4.7 mG. This result was checked by the use of a Gauss meter on loan from Bruker Instruments, and the actual magnetic fields of the four lines were measured (Figure 1). The sodium splittings as determined by the Gauss meter in the isotopically light and heavy solvents are 1.0410 ± 0.0032 and 1.0302 ± 0.0024 G, respectively. The data collected with the Gauss meter corroborate those taken from the EPR recorder, and ΔA_{Na} was found to be 10.80 ± 3.63 mG via the Gauss meter experiments. It is clear that the interaction between the naphthalene anion and the sodium cation is measurably different in THF- d_8 than it is in THF.

There are two possible explanations for the diminishing effect that perdeuteriation of the solvent has upon the interaction between the unpaired electron and the sodium cation: (1) The magnitude of $A_{Na'}$ in eq 2 is smaller in THF- d_8 than it is in THF, and/or (2) the equilibria depicted in reaction 1 is shifted to the right in THF- d_8 relative to THF. It should be pointed out that this argument is true even if the stages of ion association are more complex than indicated by reaction 1. Since $A_{Na'}$ represents the coupling constant for a contact ion pair, it does not seem reasonable that this value would change upon deuteriation of the solvent, but this can be proven only if a solution of the contact ion pair could be isolated. Due to the thermal instability of the anion radical, it is impossible to increase the temperature sufficiently to shift the equilibrium far enough to the left to allow a direct measurement of $A_{Na'}$.

In hexamethylphosphoramide (HMPA), the rate of formation and dissociation of the ion pair is often slow on the EPR time scale, allowing anion radical ion pairs to be observed simultaneously with the free ions.⁶ The ion pair of naphthalene cannot be formed in HMPA, but ion pairs of more polarizable systems can be generated via the addition of sodium salts to the anion radical solutions.⁷

The reduction of benzophenone ($C_{13}H_{10}O$) in HMPA or perdeuteriated HMPA on a sodium mirror results in the formation of an anion radical that is free of ion association.⁸ The addition of 0.01 M NaI to this solution, however, results in the formation of the ion pair, which can be observed simultaneously with the free unassociated ion. Upon increasing of the NaI concentration to 0.069 M, the spectrum for the free ion is totally replaced by that of the ion pair. When the first two lines of this ion pair were recorded in the same manner as that described for the naphthalene system, it was found that the sodium splitting does not measurably vary when HMPA is replaced with perdeuteriated HMPA.

Since the observed sodium splitting of $C_{13}H_{10}O^{\cdot-}, Na^+$ in HMPA with added NaI represents that of the ion pair only ($A_{Na'}$), a change in this value upon perdeuteriation

of the solvent would reflect a change in $A_{Na'}$. The fact that $A_{Na'}$ is independent of perdeuteriation of the solvent to some extent supports our earlier presumption that substitution of the solvent by its perdeuteriated analogue does not alter the magnitude of the sodium coupling in the tight ion pair, but rather perturbs the equilibria involving the stages of ion association.

If we consider the amount of free ion in THF to be very small, K_{eq} for $C_{10}H_8^{\cdot-}, Na^+ \rightleftharpoons C_{10}H_8^{\cdot-} // Na^+$ can be written in terms of the splittings for the two ion pairs and the observed sodium splitting. Taking 1.5 G for $A_{Na'}$ (a lower limit) and 0.0 for A_{Na} , $K_{eq} = (1.50 - A_{Na})/A_{Na}$. In THF- d_8 this can be calculated in the same way, and $K_{eq(THF-d_8)}/K_{eq(THF)} = [(1.500 - 1.0302)/1.0302]/[(1.500 - 1.0410)/1.0410] = 1.034$, which corresponds to 20 cal/mol for $\Delta G^\circ_{(THF)} - \Delta G^\circ_{(THF-d_8)}$. This value is just an estimation of the solvent isotope effect. However, even if Hirota's^{4c} estimate of $A_{Na'}$ is very low and the actual value is as high as 2.0 G and ΔA_{Na} is at its lower limit of 7.2 mG, the solvent isotope effect [$\Delta G^\circ_{(THF)} - \Delta G^\circ_{(THF-d_8)}$] is still 8 cal/mol. This is a lower limit of the solvent isotope effect. This solvent isotope effect is not limited to hydrocarbon anion radicals as evidenced by the fact that the sodium splitting for the anion radical of indantrione (ninhydrin) also is slightly smaller in THF- d_8 than in THF. Twenty-five independent measurements indicated that A_{Na} in the deuteriated THF is 4.8 ± 2.8 mG smaller than the splitting measured in THF at 298 K ($A_{Na} = 0.602$ G).

Due to the electron-donating nature of deuterium relative to hydrogen,¹ substitution of the hydrogens with deuteriums results in a slight increase in the polarity of the THF. This increased solvent polarity augments the solvent's ability to separate charge. It might therefore be worthwhile to keep in mind that the common practice of replacing the solvent with its perdeuteriated analogue in NMR studies of anionic species may result in very slight perturbations in the delicate interactions between the anion and gegen ion.

Before closing, we want to note that the THF and THF- d_8 samples, stored at $-15^\circ C$, did not exhibit any alterations in their respective EPR spectra over a period of several weeks. However, EPR spectra of the anion radical samples in THF- d_8 10 months after their preparation exhibited the presence of four anion radicals, those of the following: naphthalene, α -deuterionaphthalene, β -deuterionaphthalene, and α, β -dideuterionaphthalene. Computer simulation showed that there are four anion radicals present in this solution: (1) $C_{10}H_8^{\cdot-}$ ($A_{H\alpha} = 4.91$, $A_{H\beta} = 1.82$ G); (2) α - $C_{10}H_7D^{\cdot-}$ ($A_{H\alpha} = 4.91$, $A_{H\beta} = 1.82$ G, $A_{D\alpha} = 0.767$); (3) β - $C_{10}H_7D^{\cdot-}$ ($A_{H\alpha} = 4.91$, $A_{H\beta} = 1.82$ G, $A_{D\beta} = 0.284$); and (4) α, β - $C_{10}H_6D_2^{\cdot-}$. The ratios of concentrations were $[C_{10}H_8^{\cdot-}]/[\alpha\text{-}C_{10}H_7D^{\cdot-}]/[\beta\text{-}C_{10}H_7D^{\cdot-}]/[\alpha, \beta\text{-}C_{10}H_6D_2^{\cdot-}] = 1.0/0.60/0.50/0.16$. Possibly, the deuteriums had been transferred from the THF- d_8 or a decomposition product of THF- d_8 to the anion radical.

To support this evidence for the deuterium transfer from the solvent or a decomposition product of the solvent, we reduced perdeuteriated naphthalene in normal THF and stored the resulting solutions at $-15^\circ C$ and after two months they exhibited clear evidence for the presence of both α -protiated heptadeuteriated naphthalene, and β -protiated heptadeuteriated naphthalene anion radicals. There were three anion radicals present in this solution: (1) $C_{10}D_8^{\cdot-}$ ($A_{D\alpha} = 0.767$, $A_{D\beta} = 0.284$ G); (2) α - $C_{10}D_7H^{\cdot-}$ ($A_{D\alpha} = 0.767$, $A_{D\beta} = 0.284$ G, $A_{H\alpha} = 4.99$); (3) β - $C_{10}D_7H^{\cdot-}$ ($A_{D\alpha} = 0.767$, $A_{D\beta} = 0.284$ G, $A_{H\beta} = 1.90$).

Experimental Section

Identical experiments were carried out on the same days with

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both THF and THF- d_8 serving as the solvent. Freshly distilled samples of THF and THF- d_8 were added to separate evacuated glass bulbs, each containing freshly distilled sodium-potassium alloy. Both solvents were stored, with intermittent agitation, in these evacuated bulbs for 24 h to several days prior to use. Exactly 1.0 mL of the solvents was then distilled directly into graduated tubes on the separate all glass apparatuses. Each apparatus contained a sealed capillary tube charged with 4-5 mG of naphthalene and freshly distilled sodium mirror. These apparatuses were then sealed from the vacuum system and agitated so as to break the capillary tubes and expose the resulting naphthalene solutions to the metal mirrors. Identical experiments were carried out with two different samples of THF- d_8 (99% isotopic purity) that were purchased on different dates from Cambridge Isotope Laboratories. The THF was purchased from Aldrich Chemical Co.

The presence of a salt in the deuteriated solvent that is not present in the protiated solvent could result in the observation of a smaller value for A_{Na} in the isotopically heavy solvent. However, a salt impurity could not distill with solvent, and since both apparatuses were identical and charged with identical materials, the lower A_{Na} for the THF- d_8 solutions could not have arisen from this origin.

The EPR spectra were recorded with a Bruker ER-200 EPR spectrometer with a 9-in. magnet and a dual cavity system. A sample in THF was placed into the back cavity and a sample in THF- d_8 in the front cavity. Both spectra were then recorded several times, after which the samples were interchanged and the spectra recorded again. After a recording of the complete spectra to demonstrate that the species being observed was indeed the naphthalene anion radical (Figure 1), the first two lines of each spectra were recorded using a 1.2 or 1.4 G sweep width. After correcting for the cavity bias, this small scan range allowed the accurate determination of the sodium splitting. A cavity bias in our spectrometer system of 1.90 mG was found. That is, splittings in the back cavity were found to be 1.90 mG larger than those in the front cavity for identical samples, but the distance between the first two lines of the THF samples was found to be larger than that for the THF- d_8 for all recordings regardless of the relative sample positions.

For the experiments carried out with the Gaussmeter (a Bruker NMR Gaussmeter Model ER 035 M), the magnetic field was recorded when the recorder pen was in the center (at the point it crossed the base line) of each of the four ($m = -3/2$ and $m = -1/2$ for the samples in THF and THF- d_8) first derivative lines. The scan was stopped at these four positions, and the field as indicated by the Gaussmeter was recorded.

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Chiral Heterocyclic Ligands. 7. Syntheses of Some Chiral 2,6-Di-*N*-pyrazolylpyridines

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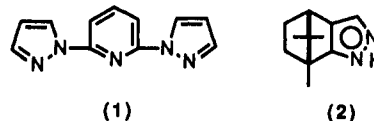
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2,2'-Bipyridine (bpy)¹ and 2,2':6',2''-terpyridine (terpy)² have long been extensively employed as bidentate and tridentate chelating ligands in both preparative and analytical coordination chemistry. More recently, many related ligands have been synthesized in which one or both of the pyridine rings of bpy are replaced by other five- or six-membered aromatic nitrogen heterocycles.³ Such re-

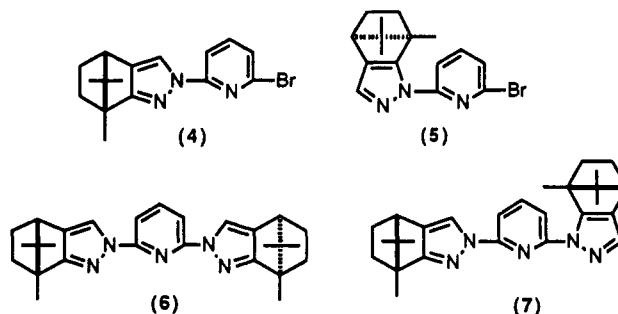
placements can significantly modify the properties of the resulting complexes, and it is now possible to tune, in a predictable manner, the ground- and excited-state properties of complexes such as the well-studied Ru(bpy)₃²⁺ complex by replacing one or more of the bpy ligands with other biheteroaromatics.^{3,4}

Planar tridentate terheteroaromatic analogues of terpy are less common. Very recently, however, the syntheses of 2,6-di-*N*-pyrazolylpyridine (1) and a number of sub-



stituted derivatives were described.⁵⁻⁷ We had also prepared a number of these ligands and confirm the physical and spectroscopic properties reported by Jameson and Goldsby.⁵ In addition, we have prepared a number of chiral derivatives of 1 for potential use as chiral auxiliaries in asymmetric catalysis. As part of ongoing studies of new chiral heterocyclic ligands⁸ and of pyrazole-containing ligands,⁹ we now report the syntheses and properties of these new ligands that were prepared from the homochiral camphor-derived pyrazole 2.^{8,10}

Reaction of 2,6-dibromopyridine (3) with 4 equiv of the sodium salt of the anion of 2 in refluxing THF gave a mixture of four products that were separated by radial chromatography and identified as the two isomeric monosubstituted products 4 and 5 and the two disubstituted



products 6 and 7. The two isomers 4 and 5 were distinguished by NMR spectroscopy, which has previously⁸ been used to differentiate between the products of alkylation of each of the two nonequivalent nitrogens of 2. This was also used to identify the symmetrical product 6, which, like the major monosubstituted product 4, results from preferential reaction of the less hindered nitrogen. The C_2

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